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ASSESSMENT OF FLUIDIZED-BED COMBUSTION SOLID WASTES FOR LAND DISPOSAL

Volume 2. Appendices A Through C

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Waste Disposal	Desulfurization	Stationary Sources		07A, 07D
Combustion	Earth Fills		21B	13C
Fluidized Bed	Linings			11G
Processing	Sorbents		13H	
Coal			21D	

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Abstract

The report, including 10 appendices, gives results of: (1) an analysis of representative samples of fluidized-bed combustion (FBC) wastes, (2) an assessment of the characteristics of leachates generated from the wastes under laboratory and field (landfill) conditions, (3) a characterization of the attenuation of the leachates by earth materials that are typical of disposal settings. (4) development of a way to predict the leachate generation behavior of FBC wastes under landfill conditions on the basis of laboratory test results by establishing a rigorous statistical relationship between the laboratory and field leaching results, and (5) assessment of the compatibility of commonly used landfill liner materials with FBC waste leachates. FBC is an emerging energy technology that holds promise for both high efficiency of energy conversion and minimization of adverse air quality impacts. A major advantage of FBC is that high-sulfur coal can be burned without the use of flue gas desulfurization equipment to meet air quality standards. The solid residues that are generated in an FBC unit are usually larger in volume and have different properties than the typical bottom ash from a conventional boiler.

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SOURCES OF WASTE AND DISPOSAL MEDIA, DETAILED HYDROLOGIC ANALYSIS, AND CHEMICAL ANALYTICAL PROCEDURES

By:

W.M. Little, J.S. Gibson, and T.W. Grimshaw

With Contributions By:

D.L. Heinrich and R.A. Minear

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A.1 Overview

During development of the program, one of the first steps was to identify suitable sources of FBC waste and disposal media as experimental materials and to acquire these materials for the laboratory and field phases of the program. Also in the early stages of the program, a detailed analysis of the hydrologic interaction of FBC wastes in a landfill setting was performed to define the major parameters to be investigated in the program and to provide the basis for assessing future FBC waste disposal sites. Another early activity of the program development was the determination of which chemical parameters were to be analyzed and the method of analysis for each.

Sources of representative FBC solid residues were identified, and a sufficient quantity of waste sample was acquired from each for all phases of the program. In addition, six disposal media types (geologic materials from likely landfill environments) were identified, and an appropriate quantity of each type was acquired. Two criteria were used to identify suitable sources of waste and disposal media. First, the material acquired was to be as representative as possible of future disposal situations that will be encountered when FBC becomes commercially viable. Thus, the waste was to be as similar as possible to future FBC waste streams from commercial units, and the disposal media were to be representative of conditions that are likely to be encountered at future disposal sites. The second criterion was the availability of a sufficient quantity of waste and media for all laboratory and field studies.

The sources of FBC waste selected were as follows:

- Pressurized FBC: Exxon Miniplant, Linden, NJ;
- Atmospheric FBC: EPRI/B&W 6'x6' Unit, Alliance, OH; and
- Atmospheric FBC: Georgetown University Boiler, Washington, DC.

The wastes from these sources are referred to as the Exxon PFBC, Alliance AFBC, and Georgetown AFBC wastes, respectively. Six disposal media types were selected and acquired from the West Virginia, Pennsylvania, and Ohio region — shale, coal mine interburden, sandstone, glacial till, alluvium, and limestone.

To analyze the hydrologic interactions of a typical FBC waste landfill, a set of "scenario" disposal conditions was assumed. These conditions include waste treatment consisting only of hydration and heat release, dedication of the landfill to FBC wastes (i.e., no codisposal with other types of wastes), and an area or trench type of landfill.

The hydrologic interactions of the FBC waste under these scenario conditions were analyzed by tracing the flow of precipitation over, through, and below the landfill. The flow path was divided into nine steps, and the potential for leachate generation and attenuation in each step was evaluated. The interactions of leachate with cover material and liner materials were also evaluated, and the formation and migration of a ground-water contamination plume was assessed. For each of the nine steps, available methods of assessing the phenomena of interest were outlined, and the parameters of importance to this investigation were defined.

A total of 36 chemical parameters were included in the various solid sample and leachate analyses performed. These parameters were defined on the basis of previous investigations and development efforts for this program which included comparison of initial leachate compositions with various water quality standards and criteria. The primary method of analysis for the metals in solution was by inductively coupled argon plasma emission spectrometry (ICAPES). This method was supplemented where necessary for lower detection limits by atomic absorption spectrophotemetry (AAS). Other analytical methods used were glass electrode, specific ion electrode, conductivity meter, ion chromatograph, and organic carbon analyzer.

A.2 FBC Waste Sources and Acquisition

At the outset of the program, plans were made to acquire wastes from three modes of FBC operation: 1) pressurized FBC (PFBC); 2) atmospheric FBC with the recycle mode of operation (AFBC-with-recycle); and 3) atmospheric FBC with the carbon burnup cell mode of operation (AFBC-with-CBC). However, as the program progressed, the AFBC-with-CBC mode fell behind the other two in terms of overall feasibility and technological development. For this reason, and because of problems encountered with acquiring waste from a suitable source, plans were dropped for using waste from the AFBC-with-CBC mode of oepration. A source of waste from a second AFBC-with-recycle unit was identified, and wastes from this unit were substituted for AFBC-with-CBC wastes as the third waste.

Approximately 10 tons of each FBC waste type were necessary to conduct the experimental work. The wastes were collected and transported to the field site at Crown, West Virginia (see Appendix E) and to Radian's Austin laboratories. Waste was used in field cells, field permeameters, and laboratory studies.

At the time that samples were collected, the test units generating wastes were operating at steady state (meeting environmental requirements for SO_2, NO_x, and particulates), and they were operating at a reasonable combustion efficiency. The materials from the different waste streams were mixed at ratios determined by the rate of generation of each stream. Thus, it was assumed that all solid waste streams from future FBC facilities will be disposed of together and that no other material will be combined for codisposal.

A.2.1 Pressurized FBC Waste Samples

The waste source chosen for the PFBC configuration was the Exxon Miniplant at Linden, New Jersey. This waste is referred to in this report as Exxon PFBC waste. A simplified schematic diagram of the Exxon Miniplant is shown in Figure A-1. After combustion, solid material leaves the bed as overflow and as elutriant. The bed overflow is one waste stream from the unit. The elutriant goes through the first cyclone, which is reported to have an overall efficiency of 95%, and the catch is recycled into the bed. The material in the second and third cyclones is collected as waste.

The components that were used for the PFBC mixed waste were collected from the following runs:

- Bed draw, Run 79;
- Bed draw, Run 80;
- Cyclone No. 2, Run 79;
- Cyclone No. 2, Run 80;
- Cyclone No. 3, Run 80; and
- Cyclone No. 3, Run 81.

Composites of bed draw, Cyclone No. 2, and Cyclone No. 3 were first prepared. The PFBC mixed waste was then formed by mixing two parts bed draw composite, one part Cyclone No. 2 composite, and 0.1 part Cyclone No. 3 composite.

The feedstocks used during these runs were Illinois No. 6 coal from the Monterey Mine and Pfizer 1337 dolomite from Ohio. The feed size was 8x50

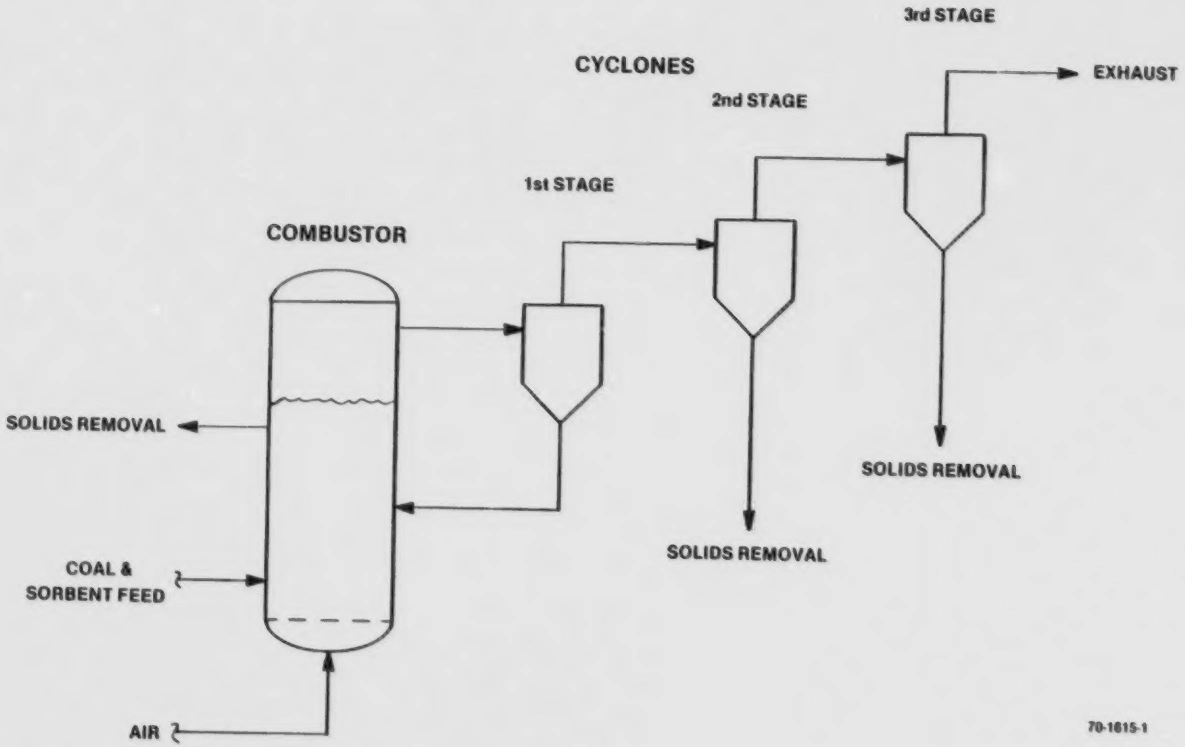

3rd STAGE
CYCLONES
EXHAUST
2nd STAGE
1st STAGE
COMBUSTOR
SOLIDS REMOVAL
SOLIDS REMOVAL
SOLIDS REMOVAL
COAL &
SORBENT FEED
AIR
70-1615-1

Figure A-1. Schematic Diagram of PFBC Unit at the Exxon Miniplant.

mesh for the coal and 8x25 mesh for the sorbent. The operating conditions for the Miniplant while the wastes were being generated are given in Table A-1.

TABLE A-1. AVERAGE OPERATING CONDITIONS FOR EXXON PFBC MINIPLANT RUNS 79, 80, AND 81

Bed Depth	2-4 m
Coal Feed Rate	130 kg/hr
Air Feed Rate	21.4 m^3/min
Ca/S Molar Ratio	1.4
Temperature	925°C (1700°F)
Pressure	925 kpa (135 psi)
Superficial Velocity	1.8 m/sec
Excess Air	18-27 percent
S Removal	85-95 percent
Stack Gas Composition:	
SO_2	150-290 ppm
NO_x	56-120 ppm
CO_2	12.5-14.5 percent
O_2	3.5-5 percent

A.2.2 Atmospheric FBC Waste Samples

Samples were collected from two AFBC units, the EPRI/Babcock & Wilcox, 6'x6' unit in Alliance, Ohio, and the Georgetown University boiler, Washington, D.C. These wastes are referred to as Alliance AFBC wastes and Georgetown AFBC wastes respectively in this report. The Georgetown waste was acquired as a substitute for waste from a unit operating in the AFBC-with-CBC mode. A schematic diagram of an AFBC unit is shown in Figure A-2.

A.2.2.1 Alliance AFBC Waste

The average operating conditions prevailing during the generation of the waste sample are listed in Table A-2. The feedstocks used at the time of sample collection were Ohio No. 6 coal (8x50 mesh) and Lowellville Limestone (16x50 mesh).

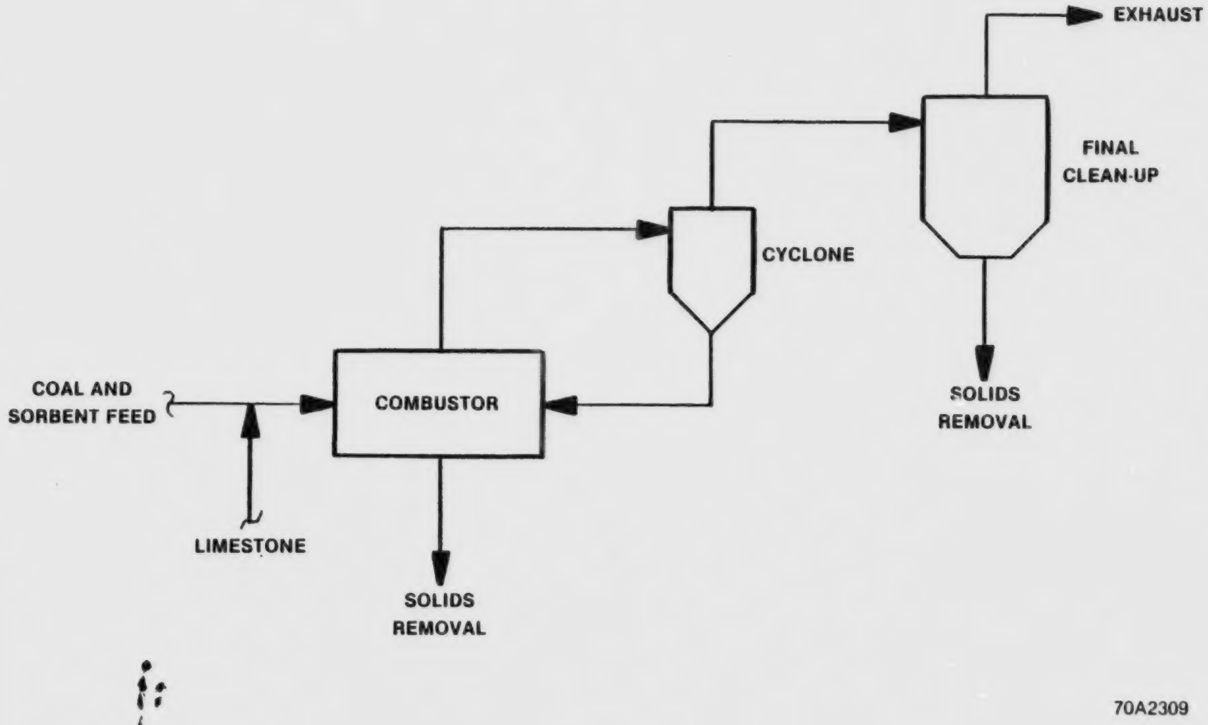

EXHAUST
FINAL
CLEAN-UP
CYCLONE
COAL AND
SORBENT FEED
COMBUSTOR
SOLIDS
REMOVAL
LIMESTONE
SOLIDS
REMOVAL
70A2309

Figure A-2. Schematic Diagram of AFBC Mode of Operation.

TABLE A-2. AVERAGE OPERATING CONDITIONS FOR THE ALLIANCE AFBC PILOT PLANT

Bed Depth	1.3 m
Coal Feed Rate	910 kg/hr
Limestone Feed Rate	460 kg/hr
Air Feed Rate	8450 kg/hr
Recycle Rate	580 kg/hr
Ca/S Molar Ratio	3.3
Temperature	844°C (1550°F)
Superficial Velocity	2.6 m/sec
Excess Air	18 percent
S Removal	77 percent
Stack Gas Composition	
SO_2	831 ppm
NO_x	—
CO_2	15.5 percent
O_2	3.3 percent

The components used to prepare the mixed Alliance AFBC waste were bed material, cyclone ash, and baghouse catch. The composite waste was formed by mixing four parts bed material, 2.5 parts cyclone ash, and 1.5 parts baghouse catch.

A.2.2.2 Georgetown AFBC Boiler Waste

The operating conditions of the Georgetown University AFBC boiler when the samples were collected are summarized in Table A-3. The coal used at the time was a medium volatile bituminous coal from an unidentified mine in southwestern Pennsylvania. The coal had a volatile content of 3% and a sulfur content of 2.3%. The limestone sorbent was obtained from Flintkote Stone Products, Stevenville, Virginia. The quarry from which the limestone was obtained was not identified. At the time of sample collection, the SO_2 and O_2 instruments were not working. The unit was operating in a recycle mode, but the recycle rate could not be measured.

TABLE A-3. OPERATING CONDITIONS OF THE GEORGETOWN UNIVERSITY AFBC BOILER AT TIME OF SAMPLE COLLECTION (BOTH BEDS OPERATING)

Static Bed Height:	0.43-0.51 m
Coal Feed Rate:	1180-1360 kg/hr
Limestone Feed Rate:	540-730 kg/hr
Air Feed Rate:	unknown
Recycle Rate:	unknown
Ca/S Molar Ratio:	unknown
Temperature:	780-800°C (1430-1480°F)
Superficial Velocity:	1.4-1.5 m/sec
Excess Air:	unknown
S Removal	unknown
Stack Gas Composition:	unknown

A.2.3 Other FBC Wastes

During the initial phases of the investigation, wastes were obtained from two sources for defining several parameters of the investigation. Bed draw and primary cyclone samples were obtained from the Pope, Evans and Robbins unit at Alexandria, Virginia, and similar samples were obtained from a small FBC unit at the EPA Industrial Environmental Research Laboratory at Research Triangle Park. These bed draw and primary cyclone samples were used during program formulation to evaluate the changes in samples resulting from exposure to temperatures typical of a carbon burnup cell and to define the time of leaching in the batch equilibration studies of the laboratory protocol. The feedstocks and operating conditions are not reported because of the limited usage of the samples during the program.

A.2.4 Other Coal Wastes

Limited analysis was performed on fly ash and flue gas desulfurization (FGD) waste from the Utah Power and Light Huntington Plant. The coal used in this plant is mined in the vicinity of the plant. The composite waste was formed by mixing one part fly ash with one part scrubber sludge.

A.3 Disposal Media Sources and Acquisition

A suite of geologic materials was identified and used in the experimental studies to evaluate their effect on FBC leachate composition. These "disposal media" were selected to meet two criteria. First, the materials were selected from areas which are likely to be typical of future disposal site conditions. Second, the materials were selected to represent a broad range of geochemical and hydrologic conditions. The six disposal media selected were as follows:

- Shale, with minor sandstone;
- Coal seam interburden;
- Sandstone, with minor shale;
- Glacial till;
- Alluvium; and
- Limestone.

Within the constraints of the two principal criteria, the disposal media were acquired from the nearest available sources to the Crown, Virginia, field site (see Appendix E) because the greatest quantity of material was required for the field cells. The sources of the disposal media and the formations from which they were obtained are listed in Table A-4. These six media are a representative and relevant set of disposal site substrates.

The shale, till, sandstone, and alluvium are all widely occurring surface or near-surface materials that are representative of disposal site substrates. They constitute a general range of fine-grained (less permeable) to coarse-grained (more permeable) materials, representing both consolidated and unconsolidated strata. The limestone and interburden provide

TABLE A-4. SOURCES OF DISPOSAL MEDIA

Medium	Formation (Age)	Mine or Quarry Location
Shale	Cassville Shale Member of Dunkard Group (Permian)	39°36'N, 80°03'W (Monongalia County, West Virginia)
Interburden	Shale Parting in Waynesburg Coal (Upper Pennsylvanian)	39°36'N, 80°03'W (Monongalia County, West Virginia)
Sandstone	Waynesburg Sandstone of Dunkard Group (Permian)	39°36'N, 80°03'W (Monongalia County, West Virginia)
Glacial Till	Ground Moraine from Wisconsin Glaciation (Quaternary)	40°12'N, 83°21'W (Union County, Ohio)
Alluvium	Ohio River Valley Floodplain Deposit (Quaternary/Recent)	39°31'N, 81°04'W (Ohio-West Virginia Border)
Limestone	Greenbrier Limestone (Mississippian)	39°34'N, 79°51'W (Monongalia County, West Virginia)

alkaline and acidic geochemical extremes, respectively, and they also simulate disposal in a limestone quarry or a coal mine.

The shale, sandstone, and interburden were all obtained from the Christopher No. 3 mine, Monongalia County, West Virginia, which is operated by the King Knob Coal Company, Clarksburg, West Virginia. Formations above the Waynesburg coal had been blasted and were being removed by scoop loader and truck. Material from the blasted section was being loaded out and removed to stock piles at the field site. Where the shale parting in the Waynesburg was thick enough (greater than 1 foot), it was being separated from the coal in the pit. The interburden sample, which contained a significant amount of coal fragments, was taken from a stockpile of this material.

The crushed limestone was purchased from the Greer Limestone Company, Greer, Monongalia County, West Virginia. It was acquired in two separate lots. Both lots were quarried from the Greenbrier Formation. The first lot was used only for very limited laboratory protocol studies. The results are reported by referring to Greer Limestone. Later, the field cell test matrix was modified, increasing the number of limestone-containing cells. A second lot of limestone was purchased from the same firm and utilized in both the field cells and the complete laboratory protocol. The results of these studies are reported by reference to the Greenbrier Limestone. The remainder of the first lot was discarded.

The nearest region that has undergone extensive glaciation is central Ohio. To obtain glacial till, an excavation contractor was located in Union County, north of Columbus, Ohio. An excavation project was underway in a deep Wisconsin-age ground moraine. Sufficient material was removed from the two to eight foot depth zone (avoiding the root zone) and transported to the field site. This particular till, reflective of the limestone bedrock in the area, is a high-lime till.

Extensive alluvial deposits do not occur in the upper Monongalia River Basin, the area where disposal media were acquired. The nearest source is the Ohio River Valley along the Ohio and West Virginia border. No current excavation projects were located, so stockpiled overburden from a conveniently located sand and gravel operation in Washington County, Ohio, was obtained.

A.4 Hydrologic Interactions of FBC Wastes in a Landfill Setting

As noted in the text, the focus of the program of investigation was placed on landfill disposal of FBC wastes because this method of disposal is likely to be the most widely used for future FBC operations. A detailed step-by-step analysis of the hydrologic interaction of a typical landfill was performed to define the variables and FBC waste characteristics to be investigated in the program.

It was assumed that the disposal site will be devoted solely to FBC wastes. Codisposal with other types of wastes was not considered in this program, although codisposal with certain other wastes may present distinct advantages in the same way that mixing and codisposal of ash from conventional coal-fired boilers with sludge from flue gas desulfurization equipment increases the stability of both wastes.

Section 2.0 of the text set forth a "scenario" landfill to provide a context for the investigation. This scenario is used here to provide the setting for the hydrologic analysis. In the scenario condition, the solid residuals generated in FBC combustors will be brought to ambient temperature before temporary storage at the plant site. From temporary storage the wastes will pneumatically loaded at appropriate intervals into closed tractor-trailer type trucks and will be hauled to the treatment/disposal site.

At the disposal site, the wastes will be removed from the trucks and again placed in temporary storage containers, such as silos. From the silos the wastes will be transferred to a treatment facility where water will be added in the proper stoichiometric amounts so that hydration reactions and resultant heat release can occur under controlled conditions. The primary purpose of this treatment step is to prepare the wastes so they can be safely disposed in a hydrated and thermally stable form. It is assumed that after treatment the wastes will still be in a solid form suitable for landfill disposal; pond disposal is assumed to be unnecessary and undesirable.

After treatment, the FBC wastes will be transported to the landfill for final emplacement. If an FBC waste disposal site is operated as a traditional landfill, then its geometry can be postulated as noted in the text (p. 2-3). For a landfill constructed according to these scenario conditions, a typical vertical section would consist of the following layers or components:

- Final cover material comprising two or more feet of soil for the site vegetation;

- Upper liner (optional), which is a moisture barrier above the waste body; it may be natural material (such as clay) or organic-based synthetic membrane;

- FBC waste layer;

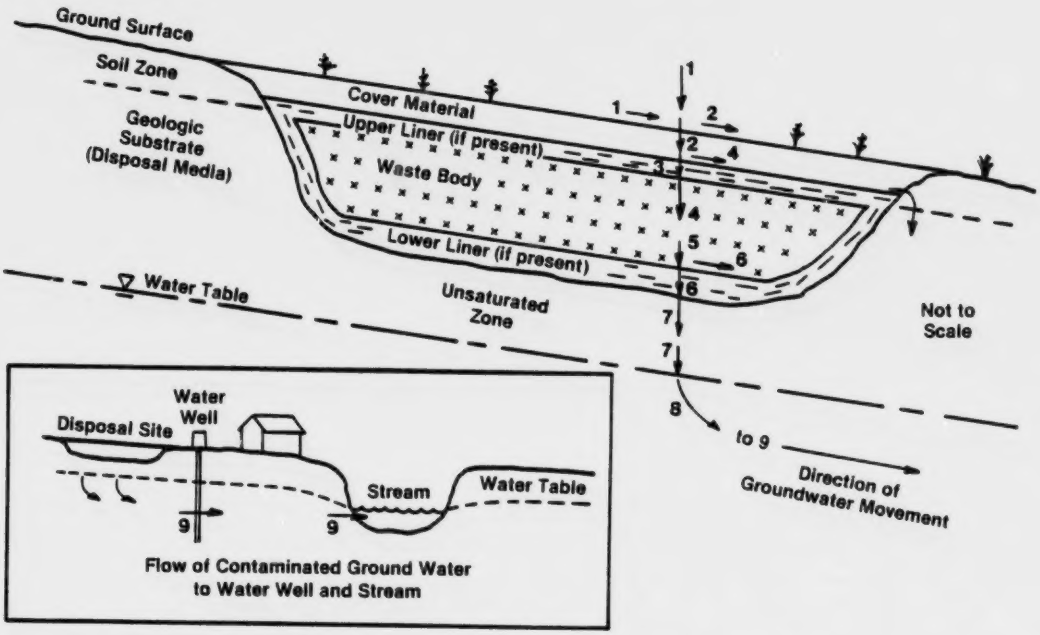
- Lower liner (optional), which is a natural or artificial barrier to downward moisture (leachate) movement, and may incorporate a leachate collection system;

- Unsaturated substrate material (disposal media), which consists of undisturbed site material below the landfill, but above the regional ground-water table; and

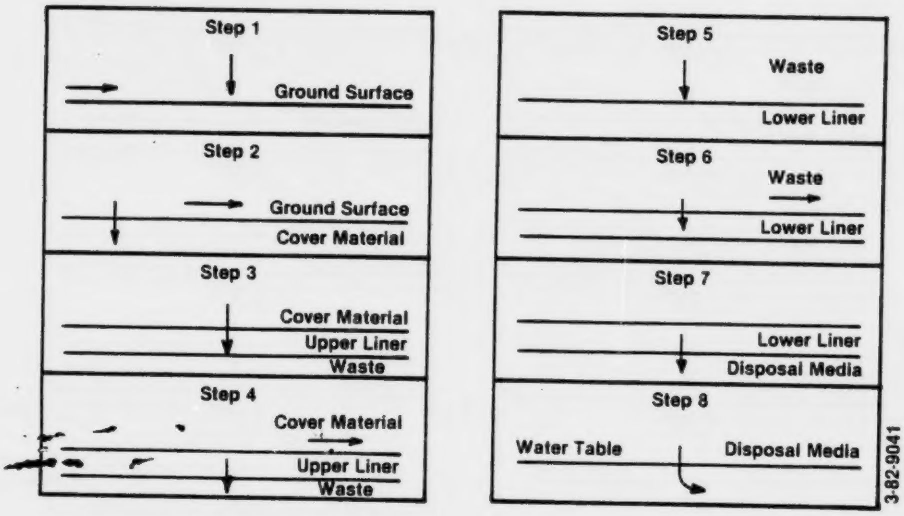
- Saturated zone of the groundwater system.

Although these idealized disposal conditions would seldom be realized in actual disposal sites, the scenario provides a means of developing a methodology for addressing disposal problems at individual sites. Figure A-3 depicts the arrangement of the major components of an FBC solid waste disposal site. Also shown are the sequential steps of water flow into, through, around, and below the waste body and associated liners. A nine-step flow path is used as the basis for defining important variables that control hydrologic contamination and the methods of investigation to address the variables. In some cases, where analytical methods are not presently available, likely avenues of approach to the problem are suggested.

Procedures are presented below for addressing the quantity (flow) and quality of water in each step. It must be borne in mind that many solute reactions are rate-dependent. Thus, physical parameters controlling quantity of flow also control rate of flow and, indirectly, the chemical quality of flow.


Ground Surface
Soil Zone
Geologic Substrate (Disposal Media)
Cover Material
Upper Liner (if present)
Waste Body
Lower Liner (if present)
Water Table
Unsaturated Zone
Not to Scale
1
2
3
4
5
6
7
8
to 9
Direction of Groundwater Movement
Disposal Site
Water Well
Stream
Water Table
9
Flow of Contaminated Ground Water to Water Well and Stream

a. Interaction of FBC Waste Disposal Site and Its Hydrologic Environment


Step 1
Ground Surface
Step 2
Ground Surface
Cover Material
Step 3
Cover Material
Upper Liner
Waste
Step 4
Cover Material
Upper Liner
Waste
Step 5
Waste
Lower Liner
Step 6
Waste
Lower Liner
Step 7
Lower Liner
Disposal Media
Step 8
Water Table
Disposal Media
3-82-9041

b. Detailed Sequence of Steps of Water Movement

Figure A-3. Major Components of an FBC Waste Disposal Site Showing Interaction with the Hydrologic Environment.

A.4.1 Step 1: Water Contacts Upper Surface of Cover Material; and Step 2: Water Infiltrates Cover Material or Leaves Site as Surface Runoff

The source of water input to the system is precipitation falling on the site and infiltrating at the surface. Proper landfill siting and design will preclude the occurrence of other sources (surface or ground-water inflow). Therefore, the determination of water inputs to the landfill system becomes a straightforward task of determining the water balance at the land surface. Precipitation falling on the land surface (as rain or snow) will either exit the site as direct surface runoff or infiltrate into the final cover. Moisture in the cover will evaporate or be consumed by the plants growing on the site (evapotranspiration) or it will percolate below the root zone and continue downward to the waste body.

The water balance at the land surface comprises Steps 1 and 2 of the conceptual framework. These two steps together are adequately modeled by the procedure presented in Reference A-1. This EPA procedure utilizes evapotranspiration estimates made by the Thornwaite Method (Reference A-2). Rainfall is partitioned into direct surface runoff, evapotranspiration losses, and deep percolation (infiltration into the landfill mass). It is conservative in that infiltration is commonly over-estimated. This procedure has been utilized in an interactive computer program reported in Reference A-3.

An adequate description of precipitation input can usually be obtained from records of the nearest weather station. Data required are mean monthly precipitation and temperature. The U.S. Geological Survey may be able to provide spot observations of rainfall chemistry, but extensive data may not normally be available. In the absence of evidence to the contrary, rainfall may be assumed to have the composition of CO_2-saturated, deionized water.

Steps 1 and 2 are site dependent and are therefore not specifically addressed in this investigation. Water balance assessments were performed on the field cells used in the study (Appendix E), but the field cells were provided with a freeboard that prevented precipitation from running off.

A.4.2 Step 3: Fluid Moves Through Cover Material (and Upper Liner, If Present) and Contacts Upper Surface of Waste Body

Infiltrating water will then move downward through the cover and upper liner (if present). The rate of flow is controlled by the input rate (effective rainfall rate) and by the permeability of the final cover. The nature of the final cover is a design variable. That is, a suitable cover material of low natural permeability will normally be selected, emplaced, and compacted to maximum density (minimum porosity and permeability).

The final cover will normally be an agricultural soil, that is, a soil capable of sustaining good plant growth. As such, it will be low in soluble salts and low in leachable toxic elements (such as boron or heavy metals). The chemical nature of the percolate can be estimated from laboratory batch extraction, lab column, or field cell tests. In most cases, extraction or column test data plus effective rainfall (infiltration) rates will be sufficient to describe water inputs to the waste body. Where cover material is extensive, or otherwise must be considered a significant element of the hydrologic system, batch extraction or column tests should be performed. Lab extraction, lab column, and field cell tests of representative geologic media are included in this investigation.

The infiltration capacity of the final cover material will depend upon the properties of the local soils, the site design, and the operational procedures at the disposal site. Consequently this variable is not included in this investigation.

A.4.3 Step 4: Fluid Infiltrates FBC Waste Body or Moves Laterally as Subsurface Runoff

Infiltrating precipitation then encounters the top of the FBC waste mass and will flow off the surface of the waste or will flow into the waste. If it flows off, it will enter the unsaturated zone directly without passing through the waste mass. Such flow occurs when the rate of infiltration exceeds the permeability of the waste mass. If the upper surface of the waste mass is convex upward, fluid will preferentially flow around the waste. Although sequentially this is the next phenomenon of interest, it can best be considered after infiltration rates through the waste body are determined. Then, subsurface runoff rates can be quantified as a rejection rate. A month-by-month accounting (water balance) model at the upper surface of the waste body may be utilized. Because it is a site-specific variable, the partitioning of water at the top of the waste mass is not addressed in this investigation.

A.4.4 Step 5: Fluid Moves Through the FBC Waste and Contacts Upper Surface the Lower Liner (If Present)

This is the primary leachate generation phase of the process in which the infiltrating precipitation leaches soluble chemical constituents from the FBC waste mass. Inasmuch as the waste body will be a relatively slowly permeable body, the leachate exiting the waste mass will be in chemical equilibrium with the waste for most chemical parameters. It can be assumed, without loss of generality, that the waste mass is homogeneous.

The chemical makeup of the leachate is addressed in this study by both laboratory and field investigations. The permeability of the waste is measured in large field permeameters.

A.4.5 Step 6: Fluid Infiltrates Lower Liner (If Present) or is Retained by the Liner

If a landfill liner system is employed, it will delay or prevent leachate migration into the adjacent materials. The liner and its associated leachate collection system will be an engineered aspect of the disposal site. Therefore, its performance characteristics may be obtained from the design specifications. The stability of various liner materials (both bentonite clay and synthetic membranes) when exposed to FBC leachate is addressed in this investigation.

In the case of a liner composed of a clay, or a clay-rich soil, there will be a small (but non-zero) leakage rate through the liner. The effective permeability of the clay liner should ordinarily be taken as 10^{-7} cm/sec, which meets minimum design standards. The quantity of leachate passing through the liner versus that removed by the leachate collection system may be determined by a mass balance accounting system. The partitioning of flow at the lower liner is not included in this investigation.

The quality of leachate passing through a failed synthetic liner would, of course, remain unchanged. The quality of leachate passing through a clay liner would, initially, be modified by ion exchange and other "attenuation" reactions with the clay minerals present. However, the capacity of a thin liner layer to alter the leachate composition would be soon exhausted and, thereafter, the leachate would pass through unchanged. If the liner layer is of substantial thickness then it can be evaluated by the same procedures described in Step 7 below for the geologic substrate.

A.4.6 Step 7: Fluid Contacts and Infiltrates Geologic Substrate

Upon exiting the bottom of the landfill, the leachate enters the subjacent geologic materials (referred to in this study as "disposal media"). As the leachate flows through the unsaturated zone, contaminants may be removed through processes of attenuation, or the geologic materials may contribute contaminants to the infiltrating fluid. Attenuation (reduction in contaminant concentration or rate of movement) may occur, for example, by precipitation, surface adsorption, or ion exchange, among other mechanisms. If the geochemical environment is greatly altered by the leachate, such as extreme changes in pH, the disposal media may release rather than remove contaminants to the leachate (contaminant mobilization).

The leachate flow beneath the landfill should be one dimensional (vertical) and steady state or only slowly varying. Many near-surface geologic materials are more permeable than the FBC wastes and thus will be free draining. The waste mass would then act as a low-pass filter, damping out variations in infiltration and providing a more-or-less steady fluid input to the subjacent system. In the absence of large scale inhomogeneities or anisotropy, the direction of flow should be vertically downward.

The phenomena of simultaneous unsaturated fluid flow and contaminant transport are the least understood of all the system components considered within this conceptual framework. Much of this investigation is devoted to an assessment of the interaction of FBC waste leachate with disposal media.

A.4.7 Step 8: Fluid Contacts and Moves Within Ground-Water System and Step 9: Fluid Degrades Existing Ground Water and is Intercepted by Wells or Discharged to the Surface-Water System

The regional ground-water flow system beneath and surrounding the waste disposal facility receives the leachate and transports it away from the site toward areas of use or discharge to surface water. A few models exist which address a "global" contaminant transport system, such as those reported in References A-4, A-5, and A-6. The methods of solution and phenomena modeled may vary, but a "complete" solution is offered. Other systems of models consist of a separate ground-water flow model which provides an input data set to a contaminant transport model. An example is the FEMWATER/FEMWASTE model set developed at Oak Ridge National Laboratory (Reference A-7 and A-8).

A large number of numerical models of ground-water flow alone exists, many of great complexity and sophistication. Some flow models are reported in References A-9, A-10, and A-11. An independent treatment of relevant contaminant transport phenomena would be required for a complete solution.

Finally, a limited number of models exist whose principal output deals with the cheimcal relations among solutes and with a solid phase or matrix. Examples are those models reported in References A-12, A-13, and A-14. The governing flow system must be assumed or determined separately.

The movement of contaminants within a ground-water system is a site-specific phenomenon, and a reasonable approach to modeling is dependent upon the scale of flow encountered. Where the contaminant source is of the same order of magnitude as the flow system, one of the "global" models discussed above should be selected. Where a contaminant plume can fairly be said to be embedded in a regional flow, the analytical solutions presented in Reference A-15 can be adopted as a first estimate, and the chemical interactions evaluated by means of a chemical model. It is very difficult to estimate which model is most appropriate in advance since selection of a modeling approach, and hence, selection of an appropriate model is dependent upon local hydrogeologic conditions. The details of each investigation must be developed on a case-by-case basis.

Once a model has been selected, it must be calibrated to the site in question. That is, a data set consisting of the data specific to FBC wastes developed in previous steps and the hydrogeologic parameters of the disposal site itself will be used to set up the model to simulate contaminant transport. In many cases, ancillary data concerning contaminant behavior in the ground-water system may also be used. The developing literature on conventional utility solid waste (fly ash and FGD sludge) disposal will provide some of these data.

Once the contaminant transport is established, sources of ground-water withdrawal or outflow to streams may be located within the model. The distribution of contaminant concentrations with time may be developed for each use or outflow point and the impacts assessed.

A.4.8 Summary of Hydrologic Analysis

A major part of this investigation is devoted to obtaining an estimate of the type and amount of chemical contaminants that emerge from FBC wastes as well as a determination of how the leachate interacts with natural disposal media. This information can then be used in conjunction with one or more of these models to predict ground-water impacts on a case-by-case (site-specific) basis. Two approaches are used in the investigation for making an estimate of the "loading" of the ground-water system under field conditions by using the results of laboratory studies. One of these approaches is empirical (Appendix G) and the other is deterministic; that is, based on an attempt to understand the fundamental chemical phenomena involved in the lab and field studies (Appendix I). Once the "loading" of a specific site has been determined, the appropriate model can be selected, modified as necessary for specific site boundary conditions, calibrated, and then run to make a projection of the anticipated hydrologic impacts. Depending on the modeling results, the site engineering or operating conditions can be modified as required so as to make the level of projected impacts acceptable.

A.5 Parameters and Methods of Chemical Analysis

An extensive chemical analysis program was undertaken to support the laboratory and field components of the project. The samples characterized included the leachate generated from FBC wastes and media-attenuated leachates from both the field and the laboratory tests. The solids composition of both FBC wastes and the disposal media were determined by analysis after total digestion. Lab analyses were also performed on leachates from the laboratory control columns, from the lab leaching columns and from other minor parts of the laboratory investigation.

A.5.1 Parameters of Analyses

On the basis of previous investigations and as a result of development efforts for this program, an analytical screening procedure was formulated to define parameters of interest for routine chemical analysis. Leachates from Step 1 of the batch equilibration protocol (primary leachate generation) for Exxon PFBC wastes were analyzed for a broad range of parameters. Table A-5 presents the analytical results for the six replicate leachates generated. The mean sand standard deviations of the observations for each parameter are also given.

In order to determine which parameters were of potential environmental concern, the mean concentration of each parameter was compared with the primary and secondary drinking water regulations and with the Discharge Multimedia Environmental Goals for both health and ecology. (References A-16, A-17 and A-18). Chemical species that were present at levels greater than 0.1 of any regulation or criterion were selected for routine analysis. Other species of interest were also added; the total list is shown in Table A-6.

As the program progressed, the parameters of analysis changed somewhat. These changes occurred in response to the level of each parameter found in the leachate and because of improvement in the sophistication and versatility of analytical instrumentation. Some parameters were added or upgraded in frequency of analysis (chloride, lithium, sodium), some parameters were downgraded to screening priority (total organic carbon), and others were dropped entirely from consideration (arsenic, lead, mercury, selenium). Screening analyses were performed for uranium initially due to its inclusion on the ICAPES array (described below). Uranium was subsequently dropped because of the low levels encountered. A summary of the analyses performed for the major components of the program is given in Table A-7.

TABLE A-5. PRELIMINARY ANALYTICAL SCREENING RESULTS (STEP 1, SEVEN-DAY EXXON PFBC LEACHATE)

Parameter[1]	Replicate Sample Number						Mean and Standard Deviation
	1701A	1701B	1701C	1701D	1701E	1701F	
Ag	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Al	0.97	0.66	0.70	0.45	0.37	0.29	0.58±0.25
As	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
B	11	15	12	15	14	11	13±2
Ba	0.16	0.21	0.14	0.12	0.16	0.18	0.16±0.03
Be	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Ca	1600	1900	1540	1340	1660	1670	1620±180
Cd	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cl	7.4	2.5	2.6	2.6	2.0	2.4	3±2
Co	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
Cr	0.029	0.079	0.054	0.205	0.054	0.005	0.07±0.07
Cu	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
F	0.82	0.74	0.91	0.77	0.72	0.67	0.77±0.08
Fe	0.39	0.21	0.25	0.18	0.16	0.10	0.22±0.10
Hg	<0.0005	<0.0005	–	–	–	–	<0.0005
K	19	19	19	19	19	11	18±3
Li	0.06	0.06	0.06	0.06	0.06	0.03	0.06±0.01
Mg	6.3	0.89	0.58	1.6	0.75	0.62	1.8±2
Mn	0.005	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na	15.4	15.0	14.8	14.8	15.0	10.9	14±2
Ni	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
NO_2-N	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Pb	0.0020	0.0021	0.0020	0.0018	0.0024	0.0049	0.0025±0.0012
pH[2]	12.0	11.9	11.5	11.8	11.6	11.6	11.7±0.2
Se	0.012	0.013	0.012	0.012	0.013	0.009	0.012±0.001
Si	1.3	0.81	0.65	0.75	0.58	0.39	0.7±0.3
SO_4	1210	1240	1260	1240	1210	1260	1240±23
Sp.Cond.[3]	9500	9500	9500	9700	9500	9500	9530±80
Sr	2.8	4.0	1.4	1.0	2.1	2.8	2.4±1
TDS	–	3770	–	–	–	–	3770
Ti	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
TOC	1.1	–	–	–	–	–	1.1
V	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zn	0.09	0.21	0.30	0.11	0.10	0.13	0.16±0.08

[1] Concentration in mg/L except as noted.

[2] Units are standard pH units.

[3] Units are micromhos/cm

TABLE A-6. LIST OF CHEMICAL PARAMETERS INCLUDED IN CHEMICAL ANALYSES

Aluminum
Arsenic
Barium*
Beryllium
Boron*
Cadmium*
Calcium*
Chloride
Chromium*
Cobalt*
Copper
Fluoride*
Iron*
Lead
Lithium*
Magnesium
Manganese
Mercury*
Molybdenum
Nickel*
pH8
Potassium*
Selenium*
Silicon*
Silver*
Sodium
Specific Conductance
Strontium
Sulfate*
Titanium
Total Dissolved Solids*
Total Inorganic Carbon
Total Organic Carbon
Uranium
Vanadium*
Zinc*

*Selected because concentrations were greater than 0.1 times Drinking Water Standards or Multimedia Environmental Goals values in screening studies.

A.5.2 Methods of Analysis

The analytical methods for routine chemical analysis were selected on the basis of reliability, precision, and detection limits. The flexibility of the methods to determine additional species when required was also considered. The quality assurance and control program for each method is given in Appendix H.

A.5.2.1 Elemental Analysis

Analyses for elements were performed principally by inductively coupled argon plasma emissions spectroscopy (ICAPES). During initial routine analyses, atomic adsorption spectroscopy (AAS) was employed to supply complementary data for screening purposes. These AAS data were complementary in that AAS allowed determination of elements not on the ICAPES array as well as elements requiring detection lmits lower than what was available by ICAPES. The results of the AAS screening of the PFBC waste leachates and the acquisition of superior ICAPES instrumentation enabled subsequent analyses to be performed by ICAPES alone.

TABLE A-7. SUMMARY OF CHEMICAL ANALYSES PERFORMED FOR THE MAJOR COMPONENTS OF THE PROGRAM

	Laboratory Studies								Field Studies		
		Main Protocol									
Element/ Species	Whole Sample Composition	Exxon PFBC	Alliance AFBC	Georgetown AFBC	Disposal Media[1]	Control Columns[2]	Leaching Columns[3]	RCRA EP[4]	Exxon PFBC	Alliance AFBC	Control Columns
Ag	X	–	–	–	–	–	–	X	–	–	–
Al	X	X	X	X	X	X	X	–	X	X	X
As	–	X	–	–	–	–	–	X	–	–	X
B	X	X	X	X	X	X	X	X	X	X	X
Ba	X	X	X	X	X	X	X	–	X	X	X
Be	X	X	X	X	–	–	–	–	–	–	X
Ca	X	X	X	X	X	X	X	–	X	X	X
Cd	X	X	X	X	X	X	–	X	X	X	X
Cl	X	X	X	X	X	X	X	–	X	X	X
Co	X	X	X	X	X	X	X	–	X	X	X
Cr	X	X	X	X	X	X	X	X	X	X	X
Cu	X	X	X	X	X	X	X	–	X	X	X
F	X	X	X	X	X	X	X	–	X	X	X
Fe	X	X	X	X	X	X	X	–	X	X	X
Hg	–	X	–	–	–	–	–	X	–	–	X
K	X	X	X	X	X	X	X	–	X	X	X
Li	X	X	X	X	X	–	X	–	X	X	X
Mg	X	X	X	X	X	X	X	–	X	X	X
Mn	X	X	X	X	X	X	X	–	X	X	X
Mo	X	X	X	X	X	X	X	–	X	X	X
Na	X	X	X	X	X	X	–	–	X	X	X
Ni	X	X	X	X	X	X	–	–	X	X	X
Pb	–	X	–	–	–	–	–	X	–	–	X
pH	–	X	X	X	X	X	X	–	X	X	X
Se	–	X	–	–	–	–	–	X	–	–	X
Si	X	X	X	X	X	X	–	–	X	X	X
SO_4	X	X	X	X	X	X	X	–	X	X	X
Sp.Cond.	–	X	X	X	X	X	X	–	X	X	X
Sr	X	X	X	X	X	X	–	–	X	X	X
TDS	–	X	X	X	X	X	X	–	X	X	X
Ti	X	X	X	X	X	X	–	–	X	X	X
TIC	–	X	X	X	X	–	X	–	–	–	X
TOC	–	X	X	X	X	X	–	–	–	–	X
U	–	X	–	–	–	–	–	–	–	–	–
V	X	X	X	X	X	X	–	–	X	X	X
Zn	X	X	X	X	X	X	–	–	X	X	X

NOTE: Some species were not included in various parts of the program for several reasons. The principal reason was deletion of species in the latter analyses because of the findings of earlier analyses.

[1] Protocol Step 1 leaching of disposal media samples.

[2] Laboratory columns containing disposal media only, designed as controls for field cells.

[3] Laboratory columns containing wastes and disposal media.

[4] Extraction Procedure as stipulated by EPA regulations developed pursuant to the Resource Conservation and Recovery Act.

A.5.2.1.1 Inductively Coupled Argon Plasma Emissions Spectroscopy (ICAPES)

ICAPES is a multielement analytical technique which provides for the simultaneous determination of up to 40 elements. The solution to be analyzed is aspirated into an argon plasma (approximately 10,000°C) where electronic excitation occurs. As the species return to lower energy states, emisson of radiant energy occurs, and the emitted radiation is passed through an entrance slit onto a diffraction grating. The diffracted radiation passes to an array of photomultiplier tubes; each array is at a specific wave length inherent to one element. The millivolt readout for each element is compared to a calibration curve to determine the concentration of that element in the aspirated solution. All calculations are performed by a minicomputer dedicated to the ICAPES spectrometer.

Two commercially available ICAPES units were used to analyze the FBC samples. A majority of the leachate from the Exxon PFBC wastes and all leachates from the auxilliary studies were analyzed using an Applied Research Laboratories Model QA-137 air spectrometer. This instrument is equipped to determine up to 34 elements simultaneously. The leachates generated toward the end of the Exxon PFBC leaching study and all of the Alliance and Georgetown AFBC leachates were analyzed with an Applied Research Laboratories Model 34000B vacuum spectrometer. The Model 34000B provides for the determination of up to 40 elements at detection limits equal to or lower than those for the Model QA-137. Both instruments feature off-peak background corrections.

Data handling for both ICAPES units is performed by dedicated minicomputers with data storage on floppy disks. Data can be presented both by a cathode ray tube and hard copy terminals. The elements determined for FBC samples by the ICAPES method are presented in Table A-8. The typical detection limits realized are also listed. All ICAPES analyses were performed in accordance with procedures outlined by McQuaker, et al. (Reference A-19) and the Environmental Protection Agency (References A-20 and A-21). The details of the analytical quality assurance and control program are given in Appendix H.

TABLE A-8. ICAPES DETECTION LIMITS FOR ANALYSIS OF FBC LEACHATES[1]

Element	Exxon PFBC[2]	Alliance AFBC[3]	Auxiliary Studies[2,4]
Al	0.06	0.05	0.06
As	0.08	ND	ND
Ba	0.001	0.001	0.001
Be	0.0005[3]	0.0005	ND
B	0.004	0.009	0.004
Ca	0.05	0.045	0.05
Co	0.15	0.006	0.15
Cr	0.005	0.001	0.005
Cu	0.005	0.001	0.005
Fe	0.004	0.008	0.004
K	40	0.04	40
Li	0.0004[3]	0.0004	ND
Mg	0.001	0.034	0.001
Mn	0.001	0.001	0.001
Mo	0.04	0.02	0.02
Na	5	0.006	5
Ni	0.002	0.003	0.002
Pb	0.07	ND	ND
Se	0.12	ND	ND
Si	0.02	0.016	0.02
Sr	0.001	0.004	0.001
Ti	0.002	0.005	0.002
U	0.3	ND	ND
V	0.01	0.003	0.01
Zn	0.002	0.003	0.002

[1] All detection limits are in mg/L.

[2] Determinations made with Applied Research Laboratories Model QA-137 ICAPES, except as noted.

[3] Determination made with Applied Research Laboratories Model 34000B ICAPES.

[4] Step 1 leaching of disposal media, unground Exxon PFBC waste, and Huntington FGD waste.

ND = not determined.

A.5.2.1.2 Atomic Absorption Spectroscopy (AAS)

AAS was used to screen and analyze the Exxon PFBC waste leachates for elements requiring lower detection limits than ICAPES provided and for those elements not in the ICAPES array. No AAS analyses were performed on the leachates from the Alliance AFBC or auxilliary studies. The PFBC leachates were analyzed using three AAS techniques: 1) electrothermal (graphite furnace) AAS; 2) cold vapor AAS; and 3) flame AAS. The elements determined by AAS and the methods used are summarized in Table A-9.

TABLE A-9. ANALYSIS OF EXXON PFBC LEACHATES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Element	Method	Description of Model	Wavelength (10^{-7} cm)	Detection Limit, mg/L
As	EPA 206.2[1]	Electrothermal AAS, Nickel Nitrate Addition	193.7	0.003
Be	EPA 210.2	Electrothermal AAS	234.9	0.0005
Hg	EPA 245.1	Cold Vapor AAS	253.6	0.0005
Li	P-E[2]	Flame AAS	670.8	0.01
Pb	EPA 239.2	Electrothermal AAS	283.3	0.002
Se	EPA 270.2	Electrothermal AAS, Nickel Nitrate Addition	196.0	0.003

[1] Reference A-21.
[2] Reference A-22.

The AAS analyses were performed using Perkin-Elmer Models 403 and 503 atomic adsorption spectral photometers. Both instruments feature background correction capabilities (deuterium arc) and are equipped with strip chart recorders. All AAS analyses were recorded on strip charts and compared to calibration standards to determine elemental concentration. Calibration standards were prepared by diluting commercially available, certified standards (1000 μg/L) to the working range of the instrument used and element determined. EPA Quality Control Check Samples were analyzed as quality control samples at a frequency of 1 QC sample per 10 leachates. One leachate in 20 was spiked and analyzed to define spike recovery and to ensure the absence of matrix interference.

Arsenic, beryllium, lead, and selenium were determined by electrothermal AAS using the Perkin-Elmer Model 503 equipped with a Perkin-Elmer Model HGA 2000 graphite furnace attachment. The ashing and atomization times and the temperature programming used to set up the instrument for each element were those recommended by the instrument manufacturer. Prior to analysis for arsenic or selenium, small aliquots were treated with 1% nickel nitrate solution. The nickel arsenide and nickel selenide formed, respectively, during the drying stage are more refractory than either element alone. Thus, higher ashing and atomization temperatures can be employed and at the same time the loss of these elements and possible background effects are reduced.

Mercury was determined by cold-vapor AAS using the Perkin-Elmer Model 403 equipped with a 10-cm quartz absorption tube. Aliquots of the leachates were digested with sulfuric and nitric acids, potassium permanganate, and potassium persulfate. Following digestion, excess potassium permanganate was reduced with hydroxylamine. Mercury was then reduced to the metallic state with stannous chloride and purged through the absorption cell for measurement.

Lithium was not on the array of the Model QA-137 ICAPES spectrometer and was determiend by flame AAS for the Exxon PFBC leachates. The analyses were performed on a Perkin-Elmer Model 504 with an air-acetylene flame. The determination of lithium in other components of the study was performed using the Model 34000B ICAPES spectrometer.

A.5.2.2 Other Water Quality Parameters

The FBC leachates were analyzed for seven non-metallic water quality parameters using six conventional analytical techniques. All analyses were performed on unpreserved aliquots with the exception of the determinations of total organic carbon. These determinations were performed on aliquots which had been preserved with the addition of phosphoric acid to a pH less than 2.

A.5.2.2.1 pH Determination by Potentiometry (Glass Electrode)

The pH of the FBC leachates was determined potentiometrically according to EPA Method 150.1 (Reference A-21). Aliquots of unpreserved leachate were analyzed on the day leachates were generated or as soon thereafter as possible. The measurements were performed with a Corning Model 130 pH meter equipped with conventional glass and reference electrodes. The pH meter was calibrated daily at pH 7 using a commercially available buffer solution. Two other commercial buffers (pH equal 4 and pH equal 10) were used as quality control samples. All results were recorded and reported in conventional pH units.

A.5.2.2.2 Fluoride Determination by Potentiometry (Selective Ion Electrode)

Fluoride was determined potentiometrically using a selective ion electrode and the method of standard additions. The aliquots analyzed were unpreserved, and the analyses were performed witin three weeks of leachate generation. All measurements were performed with a Corning Model 130 pH meter (reading directly in millivolts) equipped with an Orion fluoride selective electrode and reference electrode.

The fluoride analyses were performed by standard methods using a procedure consistent with those outlined by Baumann (Reference A-23) and Baker (Reference A-24). A 5.0 mL aliquot of leachate was transferred to a polyethylene beaker, the pH of the leachate was adjusted to 5.25 with glacial acetic acid, and 5 mL of citrate buffer was added. The citrate buffer was added to buffer the sample as well as to release complexed fluoride and to provide constant ionic strength. The fluoride-selective and reference electrodes were immersed in the sample and allowed to equilibrate for five minutes in the magnetically stirred sample. Potential was then read and recorded. At this point, 0.5 mL of 1000 mg/L fluoride solution was added. The electrodes were allowed to equilibrate for five minutes before the final potential was measured. The change of potential was used to calculate the fluoride content in the aliquot. A 1 mg/L fluoride solution served as the quality control sample for the fluoride determination. Duplicate analyses were performed on one leachate in ten. All results were calculated and reported as concentration of fluoride in mg/L.

A.5.2.2.3 Determination of Specific Conductance

Specific conductance is the measure of the capacity of a liquid to conduct electrical current. This capacity is in turn related to the concentration of ionized species in solution. The specific conductance of the FBC leachates was measured according to EPA Method 120.1.

The conductance measurements were performed with a Labline Model 11,000 Conductivity Meter. This meter measured conductance over the range 0.01 to 1,000,000 micromhos/cm and automatically corrects conductance readings to 25°C. The conductance of the FBC leachates were determined within 24 hours of leachate generation or as soon as possible thereafter. The conductance and the temperature of the samples were measured and recorded. A 0.01 M-potassium chloride solution served as the quality control check for the conductance determinations. All results were recorded and reported in micromhos/cm at 25°C.

A.5.2.2.4 Determination of Total Dissolved Solids

The determination of total dissolved solids (TDS) was performed gravimetrically according to EPA Method 160.1. An aliquot of sample was filtered through a standard fiber filter disk and collected in a tared beaker. The filtrate was then evaporated to dryness at 180°C. The beaker was preweighed to determine dissolved mass per volume of leachate.

The TDS determinations were performed on unpreserved samples within three weeks of leachate generation. Duplicate analyses were performed on one leachate in ten. All results were calculated and reported as milligrams of solid per liter of solution.

A.5.2.2.5 Determination of Sulfate and Chloride Determination by Ion Chromatography

Sulfate and chloride were determined by ion chromatography. Ion chromatography combines two techniques, ion exchange and conductometric detection to separate and then determine ions in solution. Unpreserved aliquots were analyzed for both anions within three weeks of leachate generation. A Dionex Model 14 Ion Chromatograph was used for the determinations. The procedures employed are those recommended by the instrument manufacturer. Multi-point calibration curves were prepared daily for both anions. The quality control sample for the determination of sulfate and chloride contains 100 mg/L sulfate and 100 mg/L chloride. Duplicate analyses were performed on one leachate in ten. The analytical results for both anions were calculated and reported in mg/L.

A.5.2.2.6 Determination of Total Organic Carbon

The total organic carbon (TOC) content of the FBC leachates was determined instrumentally according to EPA Method 415.1. The leachates, preserved upon generation by addition of phosphoric acid (pH <2), were analyzed the day following leachate generation. TOC determinations were performed with a Dohrmann Model DC-54 Organic Carbon Analyzer. The TOC determination consisted of three phases: 1) wet chemical oxidation of organic carbon to carbon dioxide by ultraviolet radiation; 2) reductive pyrolysis of carbon dioxide to methane; and 3) quantification of methane by flame ionization detection. The instrument provides for linear response up to 10 mg/L carbon.

A system blank is determined daily. The instrument is calibrated daily with a 2 mg/L carbon standard prepared from potassium acid phthalate. A 10 mg/L carbon standard, also prepared from potassium acid phthalate, serves as the TOC quality control standard. All results are reported as milligrams of carbon per liter of solution.

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Appendix B

FBC SOLID WASTE AND DISPOSAL MEDIA
PHYSICAL PROPERTIES

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FBC SOLID WASTE AND DISPOSAL MEDIA PHYSICAL PROPERTIES

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B.1 Overview

Several physical properties of the FBC waste and disposal media samples were determined. The primary purpose of these effort was to provide data to support the interpretation of the observed chemical behavior of the wastes and their leachates as well as the interaction of the leachate with the disposal media.

Physical characterization of the FBC wastes included particle size analysis, specific surface area determination, specific gravity measurement, and particle surface examination by scanning electron microscope (SEM). The same physical properties were determined for the disposal media as for the FBC wastes. Additional disposal media tests included examination of unconsolidated material by binocular microscope and thin-section study of consolidated material by polarizing microscope.

The unground samples of the Exxon PFBC, the Alliance AFBC, and the Georgetown AFBC wastes had mean grain sizes of 196, 270, and 230 microns respectively. The specific gravities were 2.94 for the PFBC waste, 2.65 for the Alliance AFBC waste, and 2.42 for the Georgetown AFBC waste. The apparent bulk densities were 1.10 g/cc for the PFBC waste, 1.29 g/cc for the Alliance AFBC waste, and 1.21 g/cc for the Georgetown AFBC waste.

The PFBC ground waste used in the laboratory leaching protocol contained 57 percent particles larger than 104 microns diameter. The average particle size of the remaining 43 percent was 14.5 microns. The ground PFBC waste had a specific surface area of 0.9 m^2/gram and a specific gravity of 2.934 g/cc.

Scanning electron microscope (SEM) examination indicated the dissolution of original small fine particles during leaching and subsequent precipitation of small crystals on all three wastes. SEM study of five randomly chosen Alliance AFBC waste samples showed that good representativeness was achieved during initial sample mixing and preparation. SEM observations of leached ground and unground Georgetown AFBC waste indicated that the grinding performed for the laboratory study did not greatly affect the appearance of the leached waste under magnification.

SEM observations of the disposal media indicated physical similarities in the sandstone and shale. The limestone and glacial till appeared to have the most crytalline surfaces. Alluvium had the least crystalline surfaces but contained clay-like plates instead.

The mean grain sizes of the unconsolidated disposal media in the unground state were 90 microns for the alluvium, 74 microns for the interburden, and 12 microns for the till. The ground till used in the laboratory leaching protocol had an estimated average spherical particle size of 3.2 microns. Grinding did not greatly reduce the average particle size of the alluvium or interburden media below that of the unground samples. Other ground media had estimated average spherical particle sizes of 7.4 microns for the shasle, 8.2 microns for the sandstone, and 3.6 for the limestone.

The specific surface areas of the ground unconsolidated media were 2.77 m^2/g for the glacial till, 2.76 m^2/g for the alluvium, and 2.25 m^2/g for the interburden. The specific surface area of the ground shale was 2.72 m^2/g; for the ground sandstone and limestone, the specific surface areas were 2.75 m^2/g and 2.81 m^2/g.

As determined by binocular microscope observations, the entire shale sample was composed of three shale types ranging from clay to fine sand. The interburden was poorly sorted, containing clay size to medium sand size particles. The sandstone was composed of three types of moderately sorted sand with grains ranging in size from clay to coarse sand. The glacial till was very poorly sorted and contained particles from clay size up to 58 mm in diameter. The alluvium was poorly sorted and contained particles from clay size to the pebble size.

The textural relations and textural maturity of the media were also evaluated. The glacial till contained subrounded unconsolidated gravel, angular to rounded coarse sand, and subangular to subrounded medium sand. The alluvium contained unconsolidated gravel, subangular to subrounded very coarse sand, angular to rounded sand, subangular medium and fine sand, and angular to subangular fines. The interburden consisted of fissile shale. The sandstone contained laminated sedimentary structures and subangular to subrounded grains. The shale was fissile and contained well rounded sand-size grains of quartz and muscovite, and hematite grains. Thin-section examination of the limestone showed sparry calcite, unsorted biosparite, and fossiliferous pellet rock. Samples of ground alluvium and interburden contained almost 100 percent particles larger than 104 microns.

B.2 Methods

The methods for determining the physical properties of the FBC wastes and disposal media were somewhat different.

B.2.1 Methods of Determining the Physical Properties of FBC Wastes

The average particle size, the specific surface area, and the specific gravity of the ground FBC wastes were determined by a subcontractor, Micromeritics Instrument Corporation. These studies of ground wastes were performed on samples similar to those used in the laboratory leaching protocol (described in Appendix D). The wastes were analyzed on a SediGraph Particle Size Analyzer to determine the average particle size. The particle size distribution was determined by automatic sedimentation using low-energy X-rays to measure concentrations at decreasing sedimentation depths with increasing time. The specific surface area was determined by using an instrument which allows measurement of the amount of nitrogen adsorbed by a single particle. Using a modified, single point Brunauer, Emmett, Teller (B.E.T.) equation, the specific surface area is calculated from the surface adsorption of the nitrogen. The specific gravity was determined by an iterative technique of volume comparison (using helium for the gas) on an Auto-Pycnometer.

The particle size distributon of whole samples of unground waste is more useful for interpreting the behavior of waste in field disposal conditions. Particle size determinations of the unground waste were carried out using a nest of sieves (Reference B-1).

The apparent dry bulk density was determined by weighing a representative dried unground waste sample of known volume. The bulk density was measured in units of g/mL.

Scanning electron micrographs of representative portions of FBC wastes were obtained to determine particle morphology, particle surface characteristics, particle size range, and the degree of homogeneity with respect to particle size. An Etec Omniscan scanning electron microscope was used with a Princeton Gamma Tech Model 1000 energy dispersive X-ray fluorescence spectrometer. Scanning electron micrographs were produced under two different instrumental conditions yielding micrographs first showing low magnification of general surface microstructure and a larger number of particles, and then at higher magnification to illustrate detailed surface characteristics of specific areas and particles.

B.2.2 Methods of Determining the Physical Properties of the Disposal Media

The average particle sizes of the disposal media were also determined both before and after grinding to specifications for the laboratory leaching protocol (described in Appendix D). The ground disposal media were analyzed on a SediGraph Particle Size Analyzer by the same methods as were used for the FBC waste.

The unground media were analyzed by a variety of methods. For unconsolidated samples, particle size determination of the sand fraction was carried out by ASTM D-1140-34, Standard Methods of Soil Analysis, using a nest of sieves. The clay and silt fractions were analyzed using the pipette method given in Reference B-1. The unconsolidated materials were also studied for texture by binocular microscope examination. In the case of consolidated disposal media, sieve and pipette analysis is unfeasible, so the grain size characteristics were determined by polarizing microscope examination of rock thin sections.

The specific gravity and specific surface area were determined by the same methods that were used for the FBC wastes. The method of scanning electron microscope examination was also the same as for the FBC wastes.

B.3 Physical Properties of FBC Solid Wastes

The particle size distributions of FBC wastes were determined for one ground waste (to aid in interpretation of the laboratory data, since the lab studies were performed with ground wastes) and for all wastes in the unground condition.

B.3.1 Particle Size Distribution

Samples of whole (mixed, but unground) Exxon PFBC, Alliance AFBC, and Georgetown AFBC wastes were dry sieved to determine the particle size distribution of the "as-received" waste. The results of the sieve analyses are shown in Tables B-1, B-2, and B-3. Grain size distributoin curves for the three wastes are shown in Figure B-1. The curve for Alliance AFBC waste shows an excess in the coarser fraction. This is a result of mixing of the two waste streams, the coarser bed draw, and the finer cyclone and baghouse catch. The curve for the Georgetown AFBC waste is more balanced. The mean grain sizes of the unground Exxon PFBC, Alliance AFBC, and Georgetown AFBC wastes were 195 microns, 270 microns, and 230 microns respectively.

Analysis of the average particle size for mixed PFBC waste was also performed on samples that had been ground to the same extent as the samples used for the laboratory batch leaching protocol. In order to determine the particle size distribution, the PFBC waste was wet sieved through a 104 micron sieve prior to analysis on a SediGraph Particle Size Analyzer. Consequently, the results of the tests reflect only the particle size distribution of the fraction that is smaller than 104 microns. Approximately 57 percent of the ground watse material was found to consist of particles larger than 104

TABLE B-1. PARTICLE SIZE ANALYSIS OF COMPOSITE EXXON PFBC WASTE

Sieve Number	Sieve Size (mm)	Wt. Retained on Seive (g)	Cumulative Weight (g)	Cumulative Percent
10	>2.0	0.79	0.79	0.8
20	0.84	13.16	13.95	14.1
40	0.42	15.55	29.50	29.8
60	0.25	11.52	41.02	41.4
120	0.125	22.70	63.72	64.3
200	0.074	12.36	76.08	76.8
Pan	<0.074	23.02	99.10	100.0

TABLE B-2. PARTICLE SIZE ANALYSIS OF COMPOSITE ALLIANCE AFBC WASTE

Sieve Number	Sieve Size (mm)	Wt. Retained on Seive (g)	Cumulative Weight (g)	Cumulative Percent
10	>2.0	1.60	1.60	1.0
20	0.84	23.23	24.83	15.5
40	0.42	40.65	65.48	40.9
60	0.25	16.53	82.01	51.2
120	0.125	36.10	118.11	73.8
200	0.074	31.65	149.76	93.5
Pan	<0.074	10.35	160.11	100.0

TABLE B-3. PARTICLE SIZE ANALYSIS OF GEORGETOWN AFBC WASTE

Sieve Number	Sieve Size (mm)	Wt. Retained on Seive (g)	Cumulative Weight (g)	Cumulative Percent
10	>2.0	1.73	1.73	1.7
20	0.84	16.01	17.74	17.8
40	0.42	22.51	40.25	40.4
60	0.25	8.85	49.10	49.3
120	0.125	10.38	59.48	59.7
200	0.074	7.22	66.7	66.9
Pan	<0.074	52.95	99.65	100.0

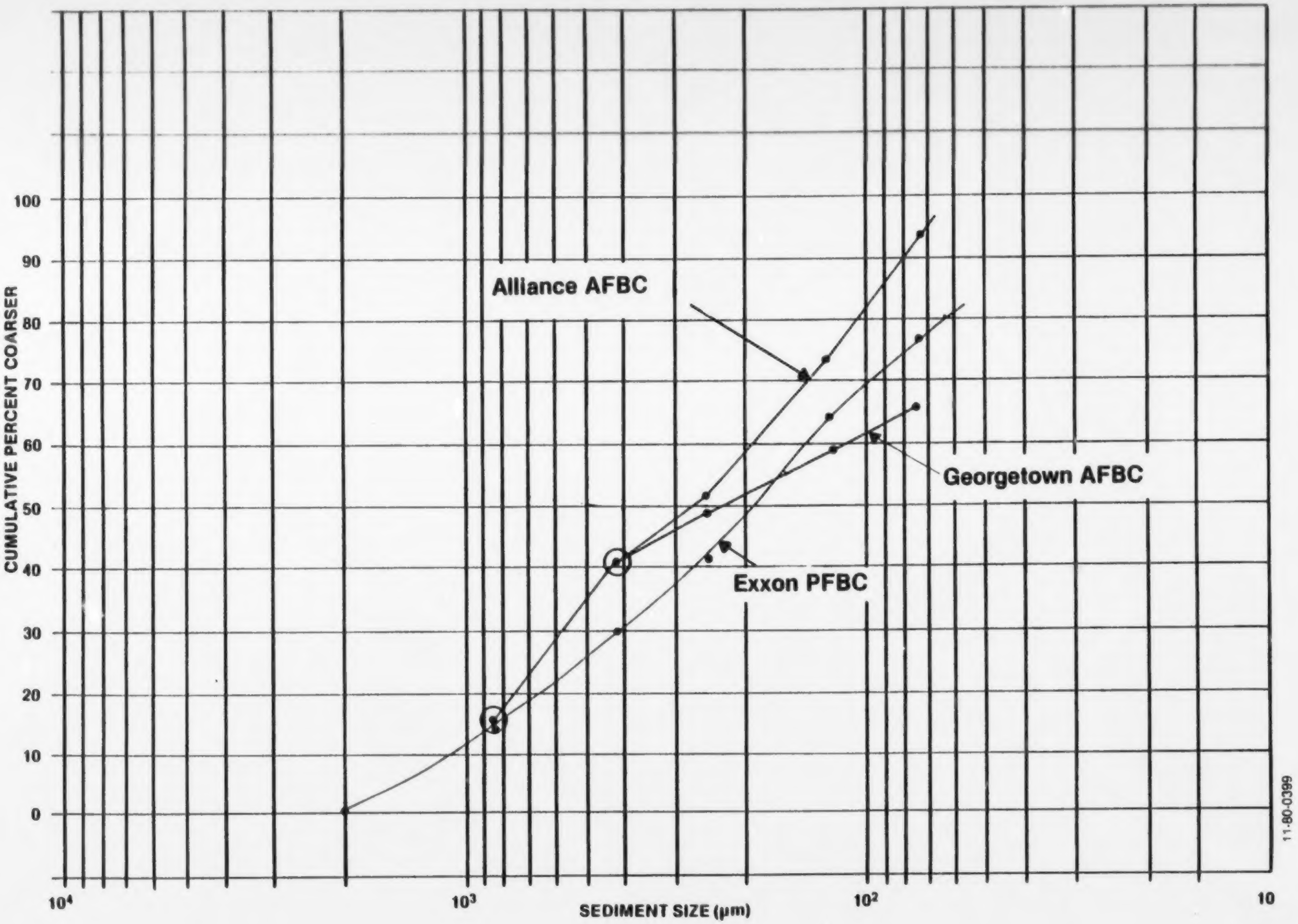


Figure B-1. Grain Size Distribution Curves for FBC Wastes.

microns. Of the remaining 43 percent, the average particle size was determined to be 14.5 microns. The particle size distribution curve for the less-than-104-micron fraction of the PFBC waste is shown in Figure B-2.

B.3.2 Particle Surface Characteristics

Scanning electron photomicrographs of Exxon PFBC, Alliance AFBC, and Georgetown AFBC wastes were prepared so that the particle surfaces could be examined. Photomicrographs were prepared of the wastes both prior to leaching and after leaching had occurred. The leached wastes were from Step 1 and seven repetitions of Step 2 of the laboratory batch equilibration protocol, which is described in Appendix D.

The scanning electron photomicrographs of PFBC waste before and after leaching are shown in Figures B-3 and B-4. Two magnifications are given for each material. These micrographs show irregularly shaped particles covered with fines before leaching and the appearance of axially longer laths after leaching. A few spherical particles are also visible in the unleached waste. Small particles can be seen on the surfaces of larger particles. Higher magnification reveals a generally irregular surface. After leaching, many laths approximately 7 to 10 microns across and 30 to 60 microns long appear in the photomicrograph with lower resolution. These laths appear to be crystals that have formed from solution during the leaching process. They may be the hydration product from calcium sulfate. A reduced number of irregularly shaped particles and a few small spheres remain. At high magnification, some of the finer materials appear to occur in thin sheets.

Scanning electron photomicrographs of Alliance AFBC waste before and after leaching are given in Figures B-5 and B-6. The unleached waste has irregularly shaped particles. Some of the particles appear to have holes like a defect-structure. A few spherical particles are visible. Particles from the leachated waste appear to be smaller, and laths are present. Many of the laths do not have the angular ends which are prevalent in the leached PFBC waste. Many particles appear to be coated with a fluffy material. Higher

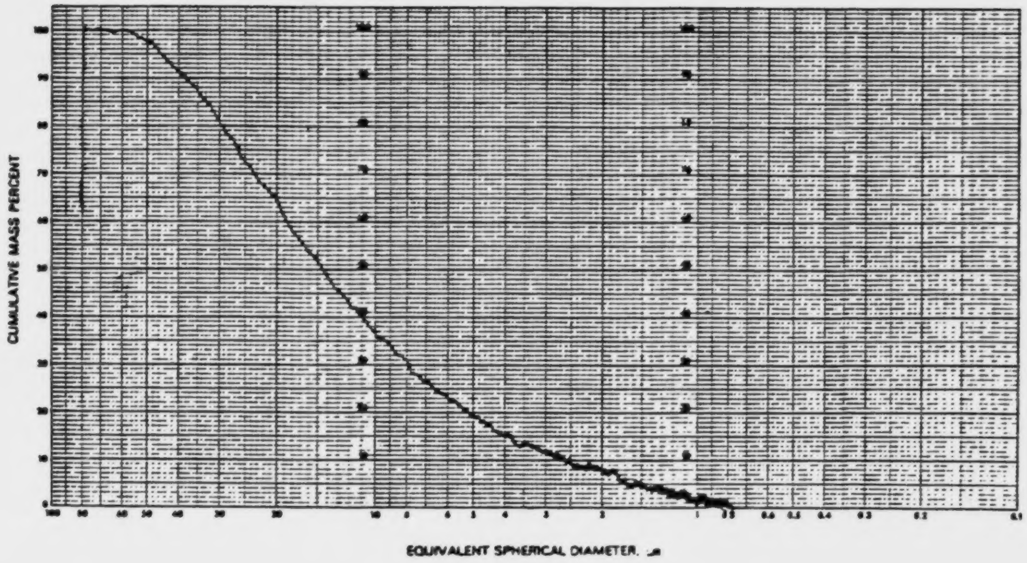
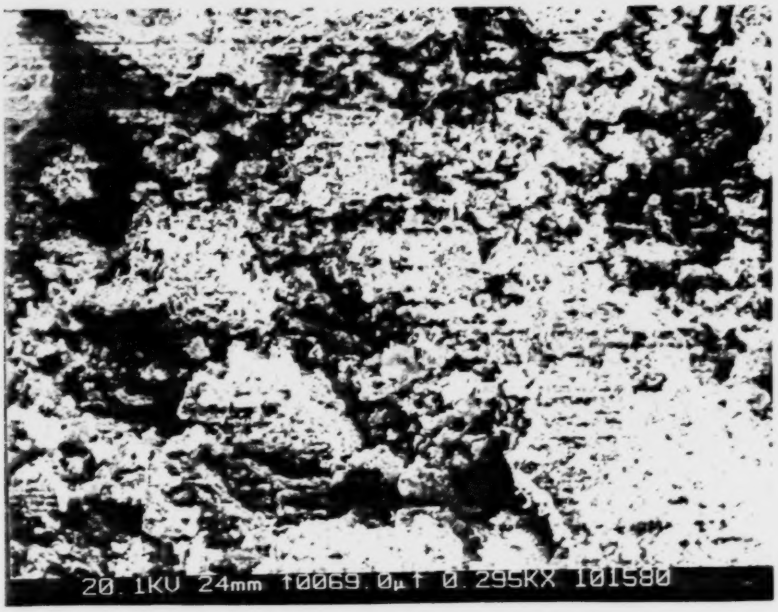


Figure B-2. Particle Size Distribution of Ground Exxon PFBC Waste (<104 Micron Fraction).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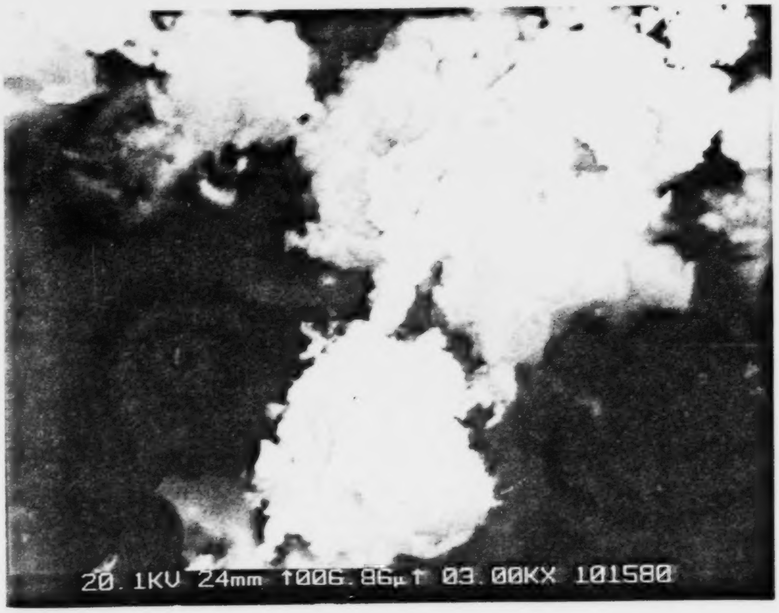
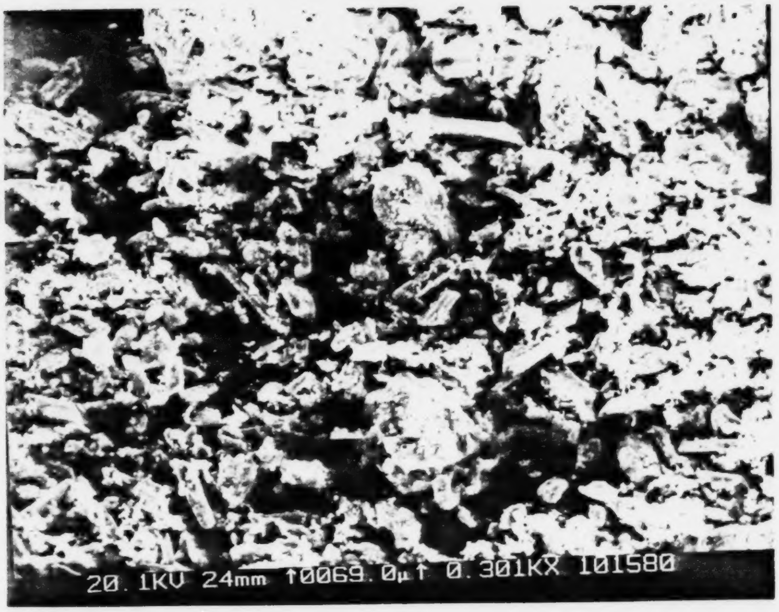
a. Magnification = 300X

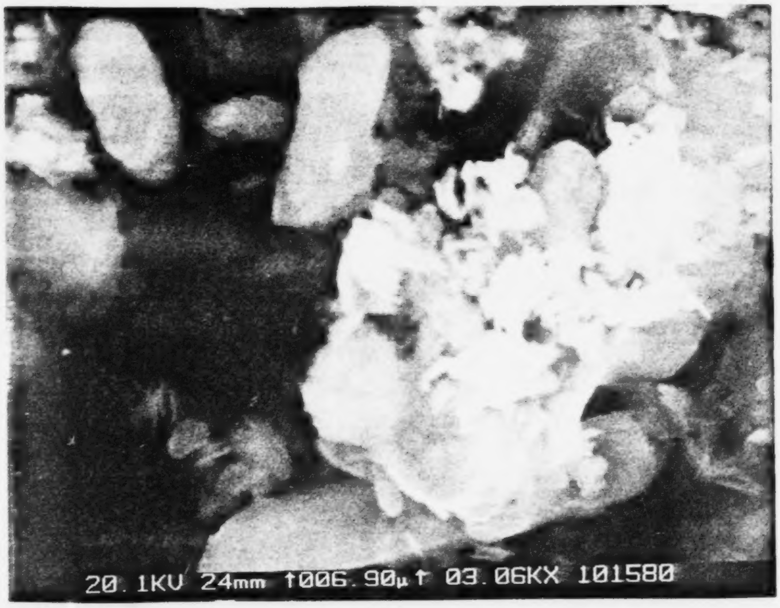

20.1KV 24mm ↑006.86μ↑ 03.00KX 101580

b. Magnification = 3000X

Figure B-3. Scanning Electron Photomicrographs of Exxon PFBC Waste Before Leaching.

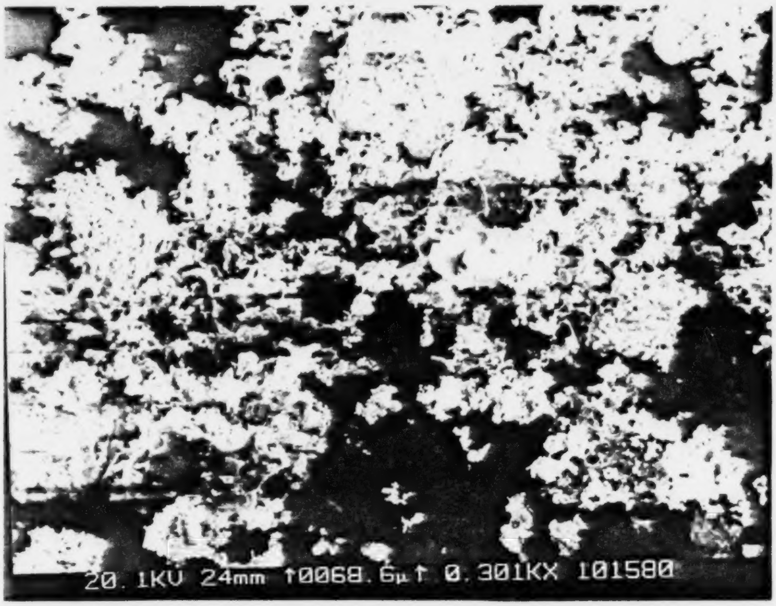

20.1KV 24mm ↑0069.0µ↑ 0.301KX 101580

a. Magnification = 300X

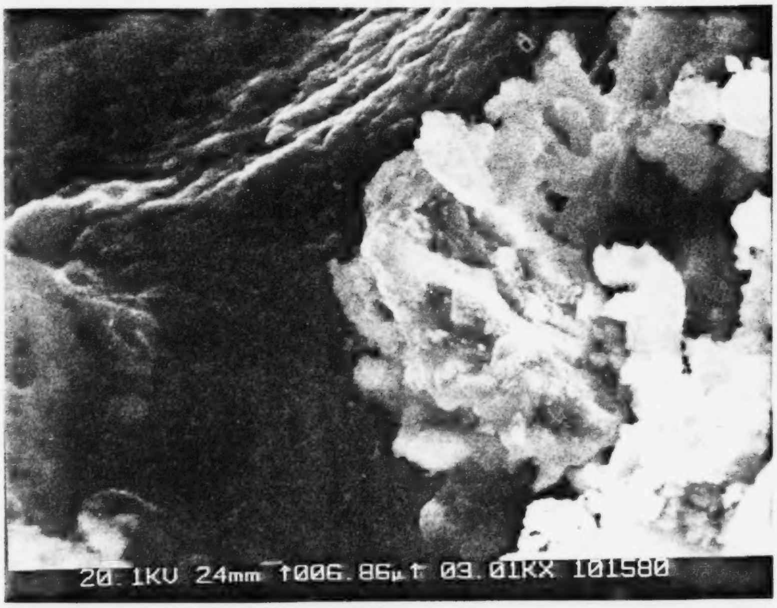

20.1KV 24mm ↑006.90µ↑ 03.06KX 101580

b. Magnification = 3000X

Figure B-4. Scanning Electron Photomicrographs of Exxon PFBC Waste After Leaching.

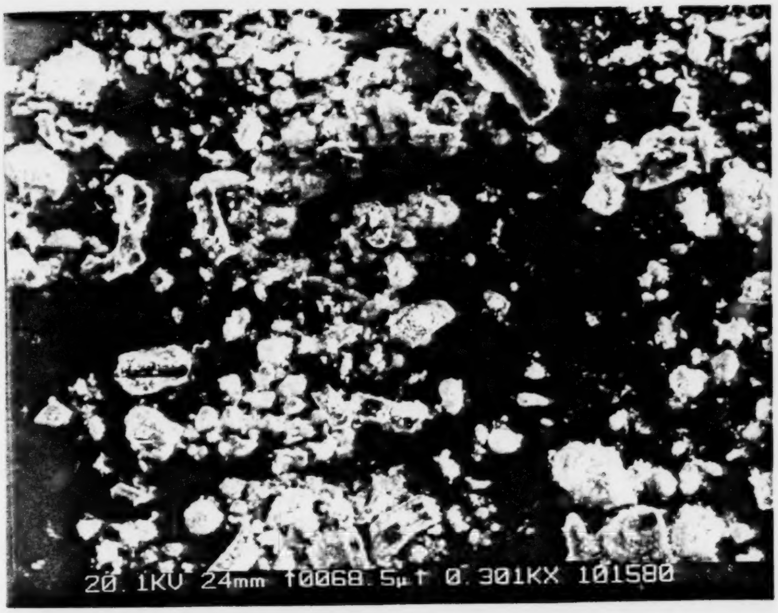

20.1KU 24mm ↑0068.6µ↑ 0.301KX 101580

a. Magnification = 300X

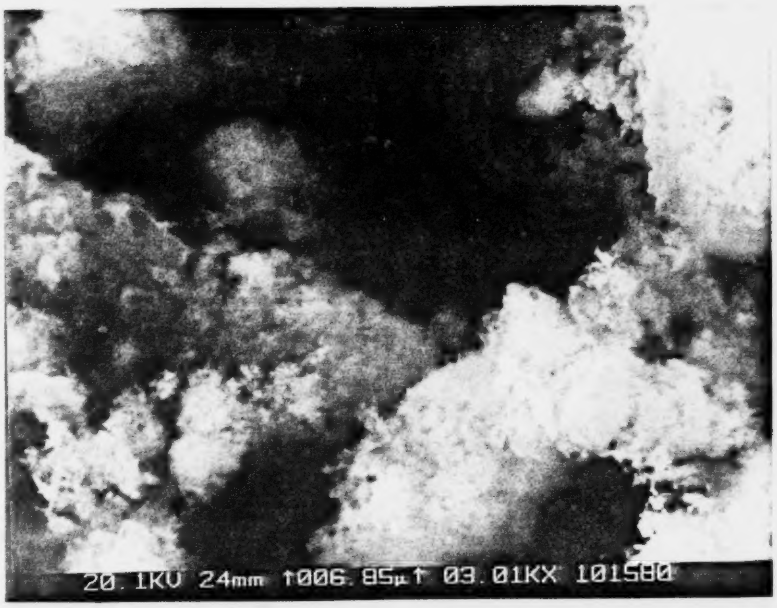

20.1KU 24mm ↑006.86µ↑ 03.01KX 101580

b. Magnification = 3000X

Figure B-5. Scanning Electron Photomicrographs of Alliance AFBC Waste Before Leaching.


20.1KV 24mm ↑0068.5µ↑ 0.301KX 101580

a. Magnification = 300X


20.1KV 24mm ↑006.85µ↑ 03.01KX 101580

b. Magnification = 3000X

Figure B-6. Scanning Electron Photomicrographs of Alliance AFBC Waste After Leaching.

magnification reveals that the fine structure of both the leached and unleached material is complex.

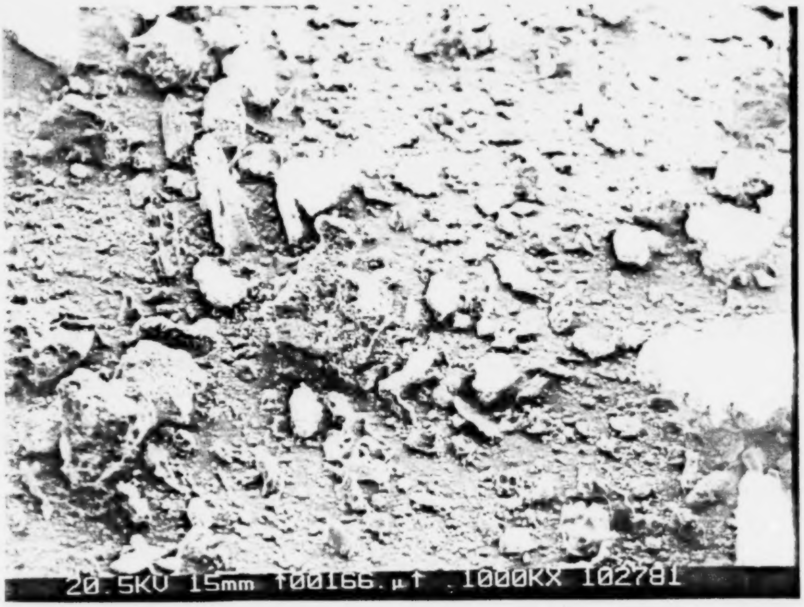
Scanning electron photomicrographs of Georgetown AFBC waste before and after leaching are given in Figures B-7 and B-8. The low magnification photomicrograph (Figure B-7a) shows that the unleached Georgetown sample is composed of two general particle sizes, one much larger than the other. The small particles probably are from the ash, whereas the larger smooth aggregates are from the bed draw. When mixed, the fines appear to adhere to the surfaces of the larger particles. After leaching (Figure B-8), the original fines appear to be absent, and small new needles are adherent to the bed draw material. The bed draw material does not appear to have undergone changes.

Figure B-9 shows the unground Georgetown AFBC waste after leaching. This material is very similar to the ground, leached waste. No large differences were noted between leached unground and leached ground waste.

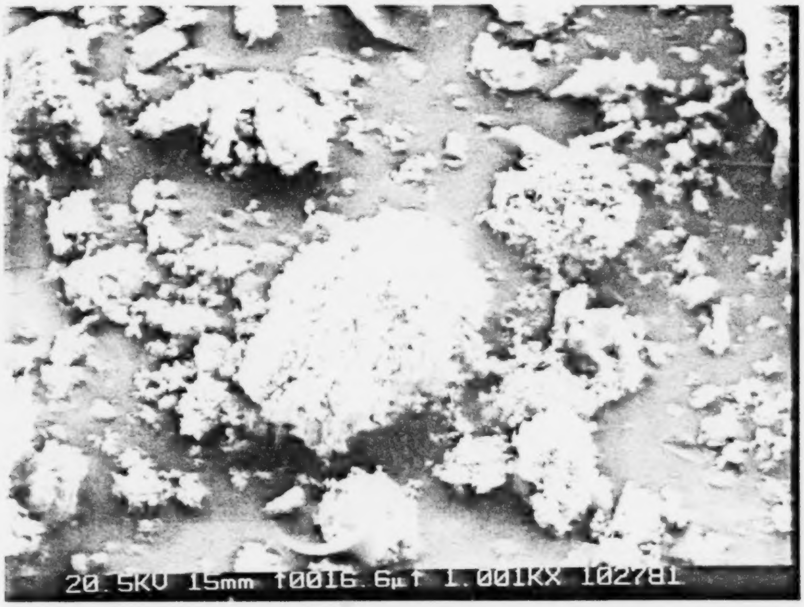
To determine how representative waste samples used in laboratory leaching were, five randomly selected samples of unleached Alliance AFBC waste were examined. At low magnification, no differences are observed among the five representative samples (Figures B-10 through B-14). When observed at higher magnification, these samples have some differences in particle size and microstructure, but in general, the randomly chosen sample lots are homogeneous and representative. No particular sample lot is characterized by a group of segregated crystal structures or particle size.

B.3.3 Specific Gravity and Apparent Bulk Density

The specific gravities for the Exxon PFBC, Alliance AFBC, and Georgetown AFBC wastes (unground) were determined to be 2.49, 2.65, and 2.42, respectively. The apparent bulk densities for these materials (ground) were 1.10 g/cc, 1.29 g/cc, and 1.21 g/cc, respectively.

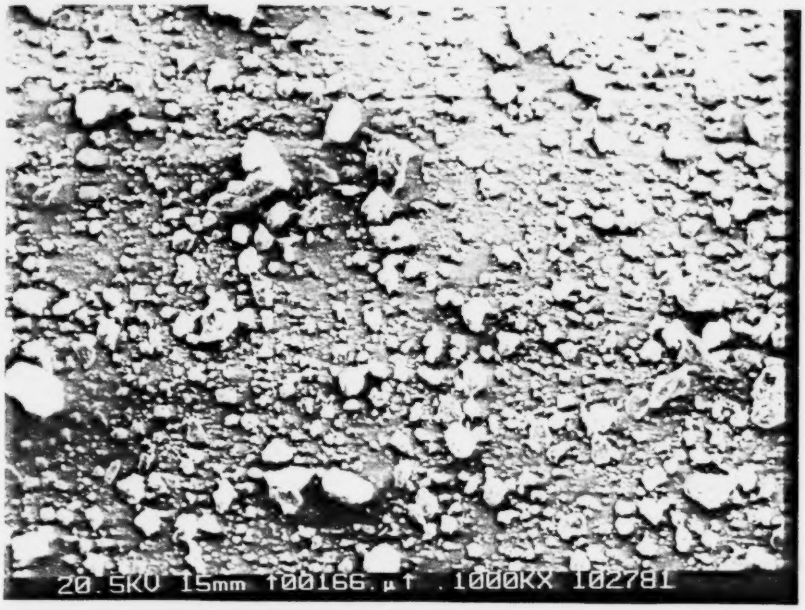

20.5KV 15mm ↑00166.μ↑ .1000KX 102781

a. Magnification = 100X

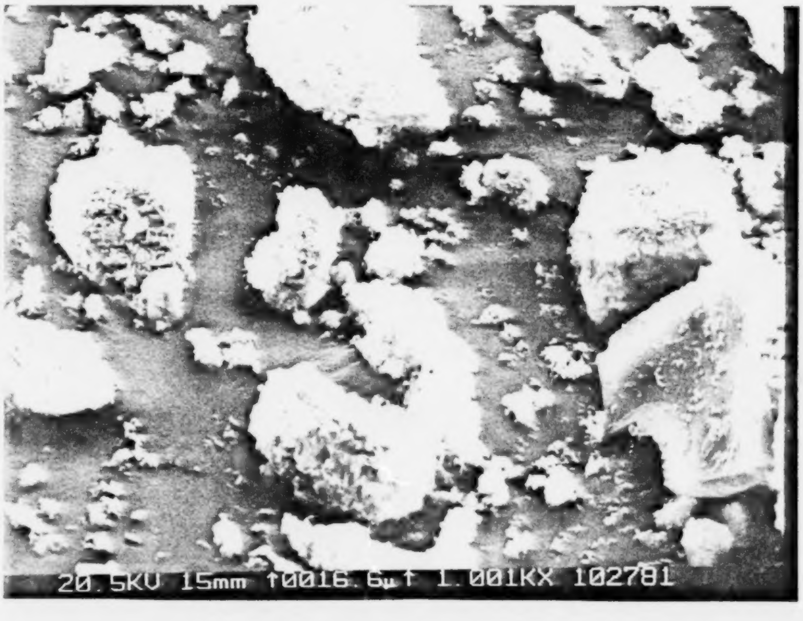

20.5KV 15mm ↑0016.6μ↑ 1.001KX 102781

b. Magnification = 1000X

Figure B-7. Scanning Electron Photomicrographs of Georgetown AFBC Waste Before Leaching.

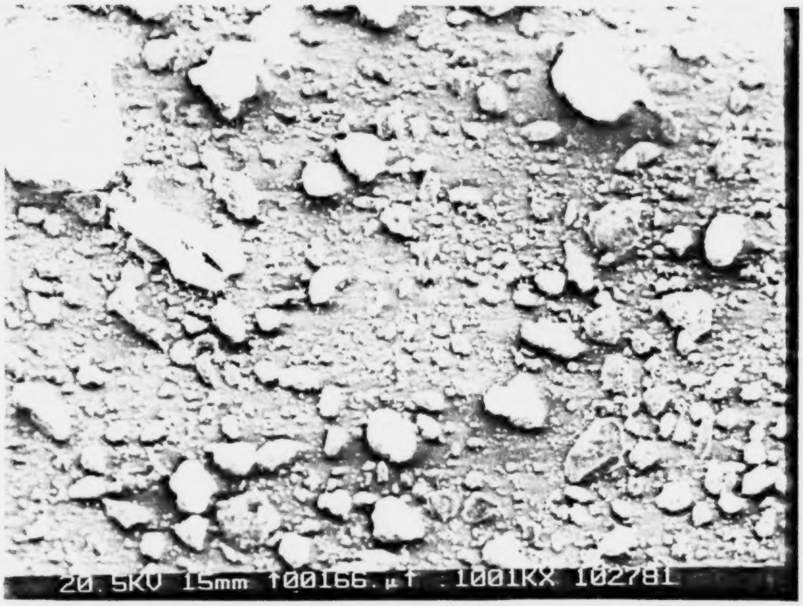

20.5KV 15mm ↑00166.μ↑ .1000KX 102781

a. Magnification = 100X

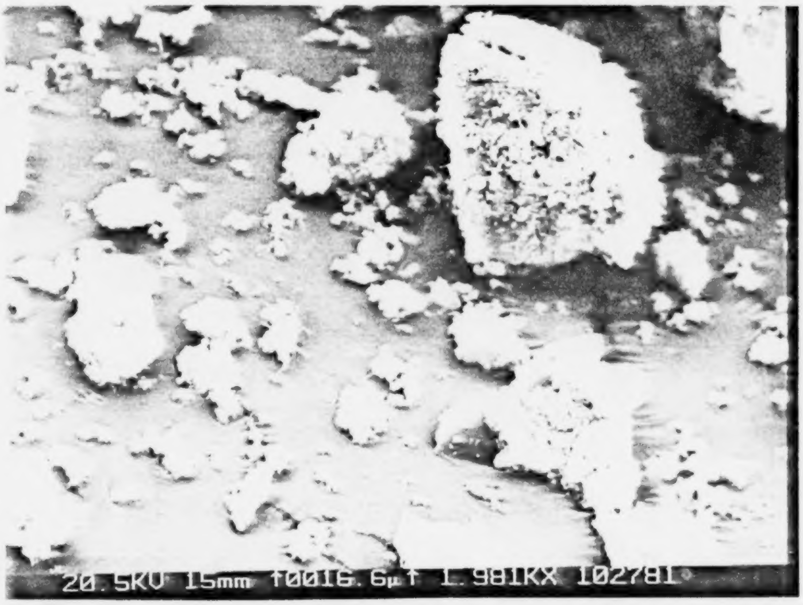

20.5KV 15mm ↑0016.6μ↑ 1.001KX 102781

b. Magnification = 1000X

Figure B-8. Scanning Electron Photomicrographs of Georgetown AFBC Waste After Leaching.

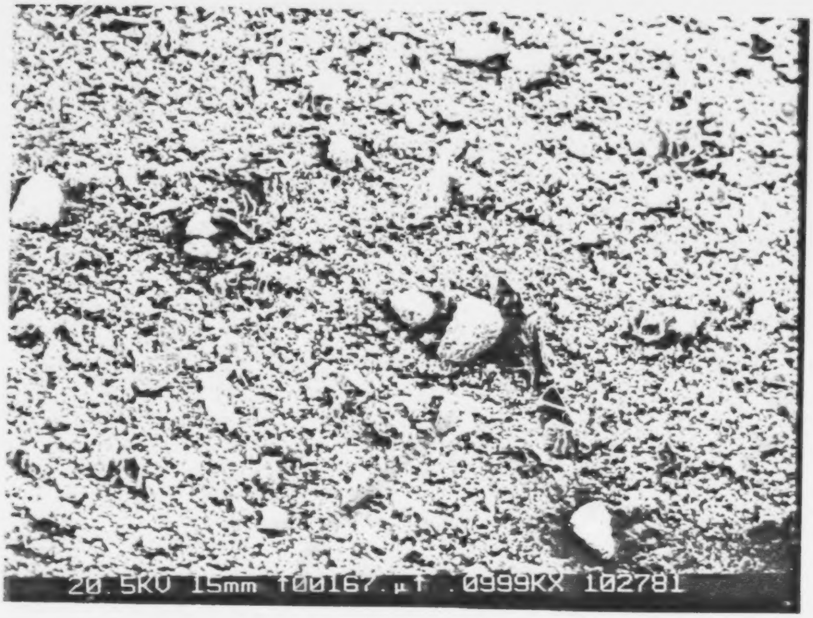

20.5KV 15mm ↑00166.μ↑ .1001KX 102781

a. Magnification = 100X

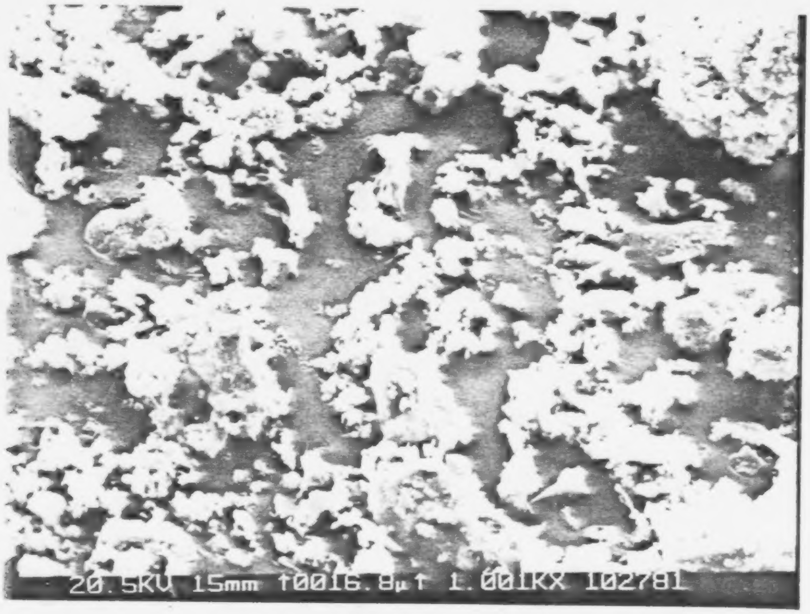

20.5KV 15mm ↑0016.6μ↑ 1.981KX 102781

b. Magnification = 2000X

Figure B-9. Scanning Electron Photomicrographs of Leached Unground Georgetown AFBC Waste.

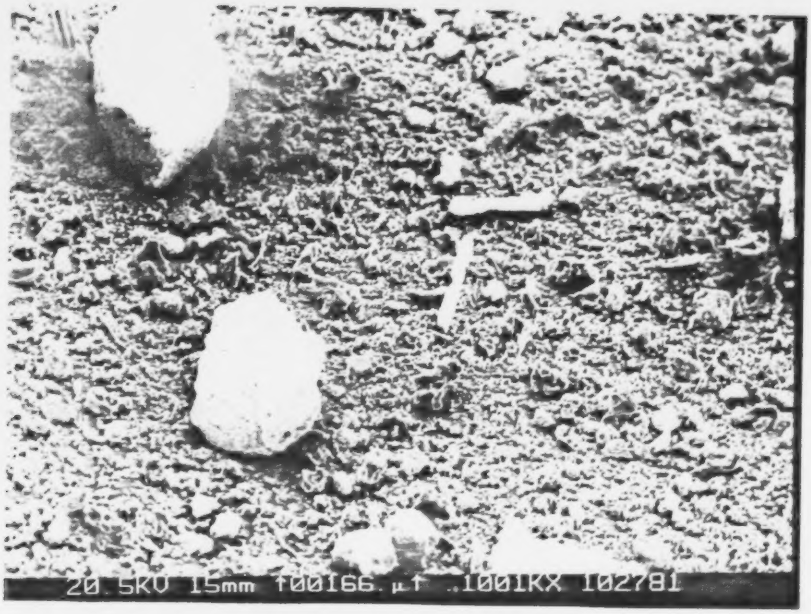

20.5KV 15mm †00167.µ† .0999KX 102781

a. Magnification = 100X

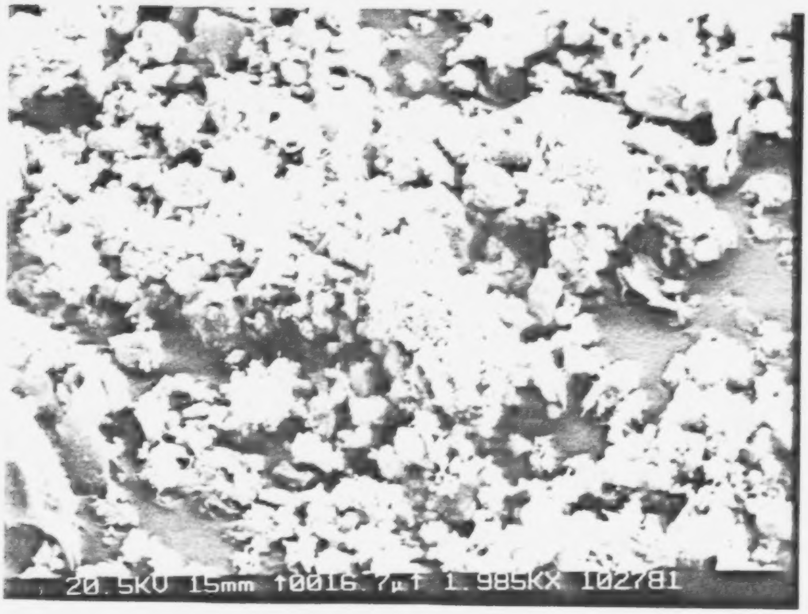

20.5KV 15mm †0016.8µ† 1.001KX 102781

b. Magnification = 1000X

Figure B-10. Scanning Electron Photomicrographs of Alliance AFBC Waste Before Leaching: Representativeness Test, Sample A.

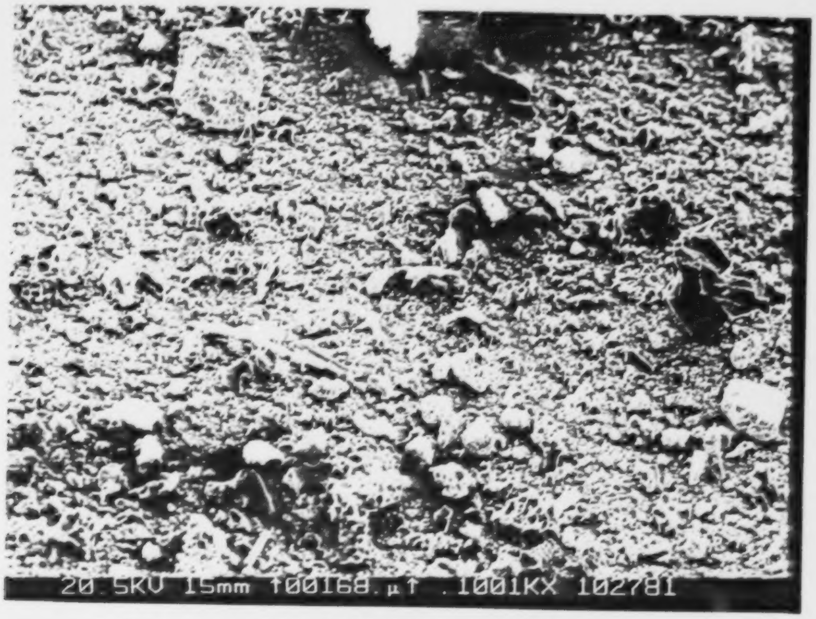

20.5KV 15mm ↑00166.μ↑ .1001KX 102781

a. Magnification = 100X

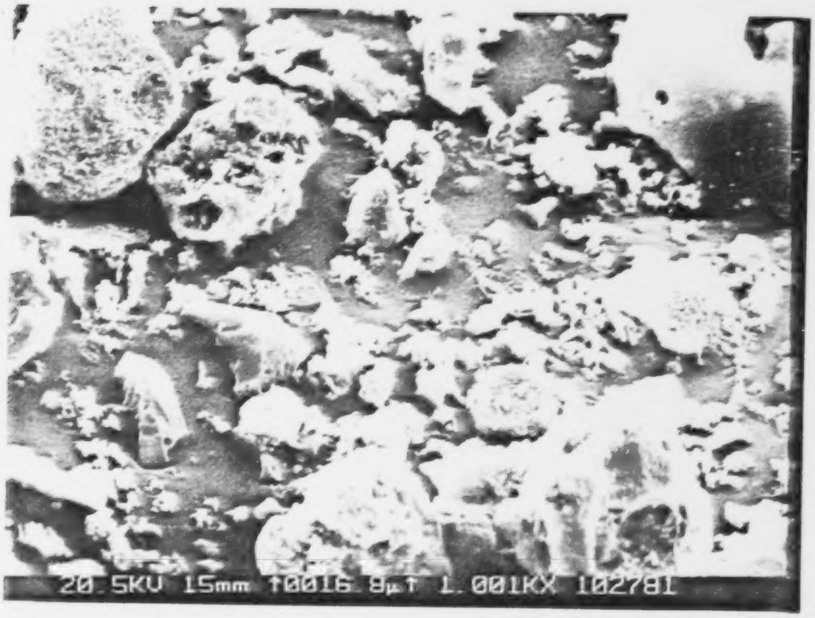

20.5KV 15mm ↑0016.7μ↑ 1.985KX 102781

b. Magnification = 2000X

Figure B-11. Scanning Electron Photomicrographs of Alliance AFBC Waste Before Leaching: Representativeness Test, Sample B.

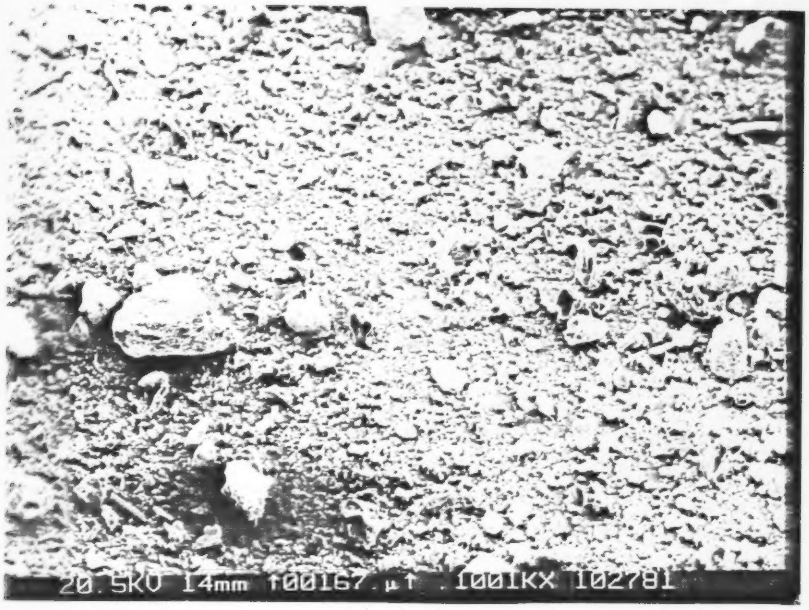

20.5KV 15mm †00168.μ† .1001KX 102781

a. Magnification = 100X

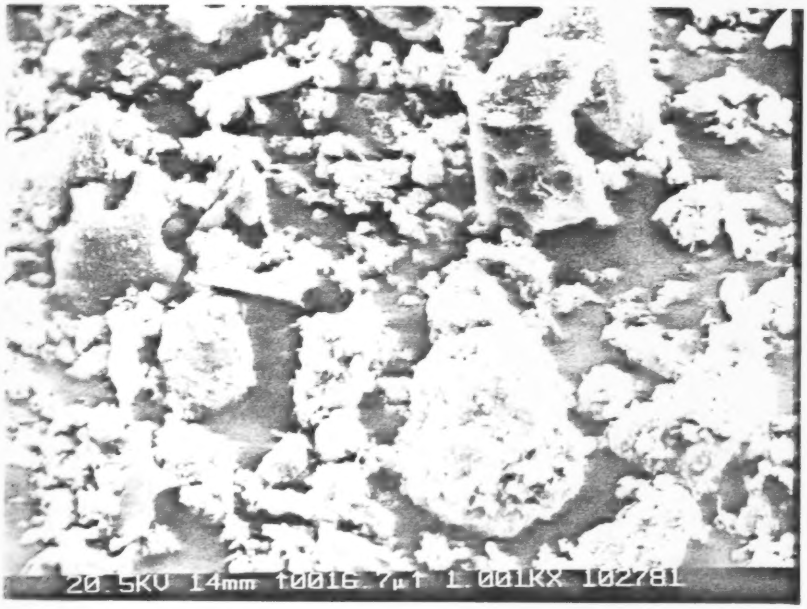

20.5KV 15mm †0016.9μ† 1.001KX 102781

b. Magnification = 1000X

Figure B-12. Scanning Electron Photomicrographs of Alliance AFBC Waste Before Leaching: Representativeness Test, Sample C.

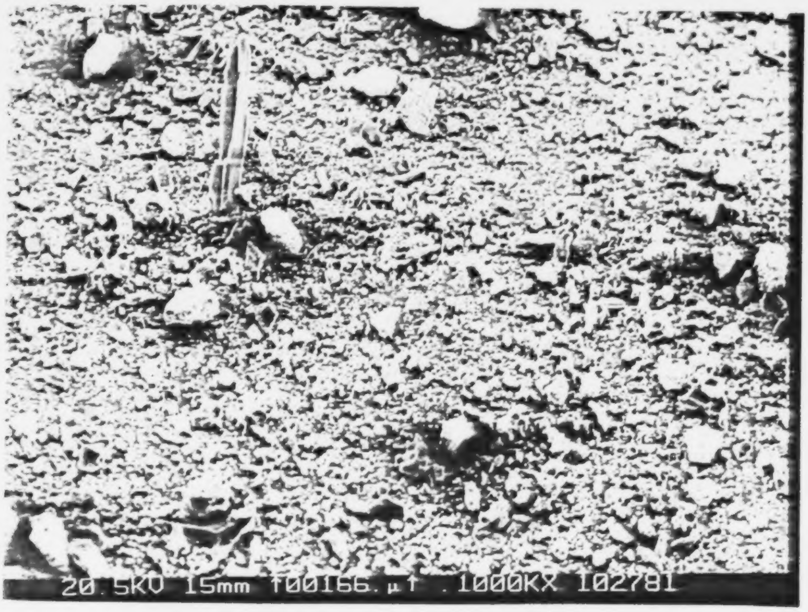

20.5KV 14mm ↑00167.μ↑ .1001KX 102781

a. Magnification = 100X

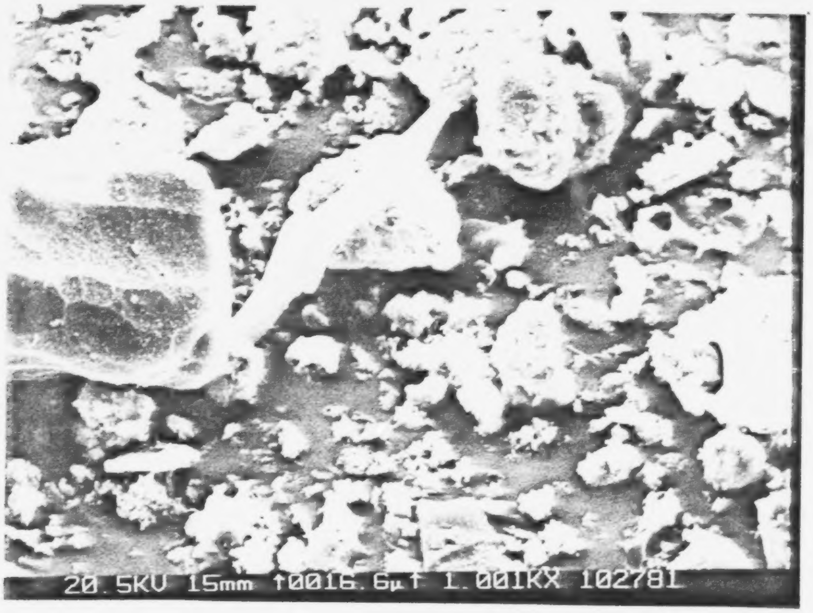

20.5KV 14mm ↑0016.7μ↑ 1.001KX 102781

b. Magnification = 1000X

Figure B-13. Scanning Electron Photomicrographs of Alliance AFBC Waste Before Leaching: Representativeness Test, Sample D.


20.5KV 15mm ↑00166.μ↑ .1000KX 102781

a. Magnification = 100X


20.5KV 15mm ↑0016.6μ↑ 1.001KX 102781

b. Magnification = 1000X

Figure B-14. Scanning Electron Photomicrographs of Alliance AFBC Waste Before Leaching: Representativeness Test, Sample E.

B.3.4 Specific Surface Area

The specific surface area was determined for the ground PFBC waste was found to be 0.9 m^2/g.

B.4 Physical Properties of the Disposal Media

The particle size distribution, specific surface area, specific gravity, and particle surface characteristics were determined for each of the six disposal media.

B.4.1 Particle Size Distribution

Separate particle size analyses were conducted for the ground and unground samples of the disposal media.

B.4.1.1 Particle Size Distribution of Unground Media

Particle size distributions were determined for the three unconsolidated media--interburden, till, and alluvium. The particle size distributions were determined by first separating the sand-size fraction from the silt and clay size fraction. The sand-size fraction analyses are given in Table B-4. The interburden sample contained the highest cumulative percent (9.1%) of granules and sand fraction. The alluvium sample contained the most silt. The till contained intermediate quantities of all size fractions.

TABLE B-4. SAND SIZE FRACTION ANALYSIS OF THREE DISPOSAL MEDIA

	Sieve Number	Sieve Size (mm)	Weight Retained on Sieve (g)	Cumulative Weight (g)	Cumulative Percent
Interburden	10	>2.00	9.03	9.03	9.1
	20	0.84	11.62	20.65	20.9
	40	0.42	7.46	28.11	28.4
	60	0.25	4.17	32.28	32.7
	120	0.125	1.93	34.21	34.6
	200	0.074	1.03	35.23	35.6
	Pan	<0.074	63.58	98.82	100.0
Till	10	>2.00	5.78	5.78	5.8
	20	0.84	3.99	9.77	9.8
	40	0.42	3.56	13.33	13.3
	60	0.25	3.10	16.43	16.4
	120	0.125	4.86	21.29	21.3
	200	0.074	4.06	25.35	25.4
	Pan	<0.074	74.75	99.9	100.0
Alluvium	10	>2.00	0.13	0.13	0.1
	20	0.84	0.07	0.20	0.2
	40	0.42	0.86	1.06	1.1
	60	0.25	7.19	8.25	8.2
	120	0.125	29.64	37.89	37.9
	200	0.074	22.50	60.39	60.4
	Pan	<0.074	39.61	100.0	100.0

The silt and slay fractions for the interburden, till, and alluvium were determined by the pipette method (Reference B-1). The results of these analyses are given in Tables B-5, B-6, and B-7 and are shown graphically in Figure B-15. The alluvium contained mostly coarse silt with some very fine sand, and about 10% clay material. The interburden contained a larger portion of fine sand than the alluvium, and about 21% clay, which was a larger clay fraction than was measured for the alluvium. The glacial till had the largest clay fraction (39.2%), and it contained the least fine sand.

The grain size and textural characteristics of the other three disposal media were determined by binocular microscope examination of sandstone and shale samples and by polarizing microscope examination of limestone thin sections. A composite description of the shale, interburden, sandstone, till, and alluvium is given in Table B-8. A thin-section descripton of the limestone is given in Table B-9.

TABLE B-5. PIPETTE ANALYSIS OF INTERBURDEN

Diameter (mm)	Withdrawal Depth (cm)	Time	Weight of Beaker (g)	Weight of Beaker + Sample (g)	Weight of Sample (g)	Corrected Weight (−0.060 g Calgon)	X 50 (g)	Cumulative Percent Coarser
0.074	20	20 sec	50.41	50.72	0.31	0.25	12.5	51.4[1]
0.044	20	1 min 45 sec	50.01	50.31	0.30	0.24	12.0	53.3
0.031	10	1 min 45 sec[2]	49.92	50.21	0.29	0.23	11.5	53.3
0.0221	10	3 min 28 sec	49.93	50.20	0.27	0.21	10.5	59.2
0.156	10	6 min 58 sec	48.68	48.94	0.26	0.20	10.0	61.1
0.078	10	28 min	48.93	49.13	0.20	0.14	7.0	72.8
0.0039	10	1 hr 51 min	49.43	49.60	0.17	0.11	5.5	78.6
0.002	10	7 hr 24 min	52.55	52.66	0.11	0.05	2.5	90.3

NOTES: Sand fraction weight = 13.22g
Total sample weight = 27.72g

[1] The percentage of material finer than 74 microns for the interburden sample is represented by two data points (36% and 51%). Due to the mixture of clay with consolidated material composing the interburden media, the sand size distribution was determined by dry sieving while the silt and clay fraction was subjected to wet sieving prior to the pipette analysis. The consolidated nature of the interburden resulted in variability in representativeness of the two samples dry sieved and wet sieved at the junction of the sand and silt/clay size fractions.

[2] Restir.

TABLE B-6. PIPETTE ANALYSIS OF TILL

Diameter (mm)	Withdrawal Depth (cm)	Time	Weight of Beaker (g)	Weight of Beaker + Sample (g)	Weight of Sample (g)	Corrected Weight (−0.060 Calgon)	X 50 (g)	Cumulative Percent Coarser
0.074	20	20 sec	50.41	50.81	0.40	0.338	16.9	25.5
0.044	20	1 min 45 sec	48.70	49.07	0.37	0.308	15.4	32.1
0.031	10	1 min 45 sec[1]	50.03	50.38	0.35	0.288	14.4	36.5
0.0221	10	3 min 28 sec	49.05	49.38	0.33	0.268	13.4	40.9
0.0156	10	6 min 58 sec	50.07	50.36	0.29	0.228	11.4	49.8
0.0078	10	28 min	48.53	48.81	0.28	0.218	10.9	52.0
0.0039	10	1 hr 51 min	48.16	48.40	0.24	0.178	8.9	60.8
0.0020	10	7 hr 24 min	49.45	49.64	0.19	0.128	6.4	71.8

NOTES: Sand fraction weight = 5.79g
Total sample weight = 22.69g

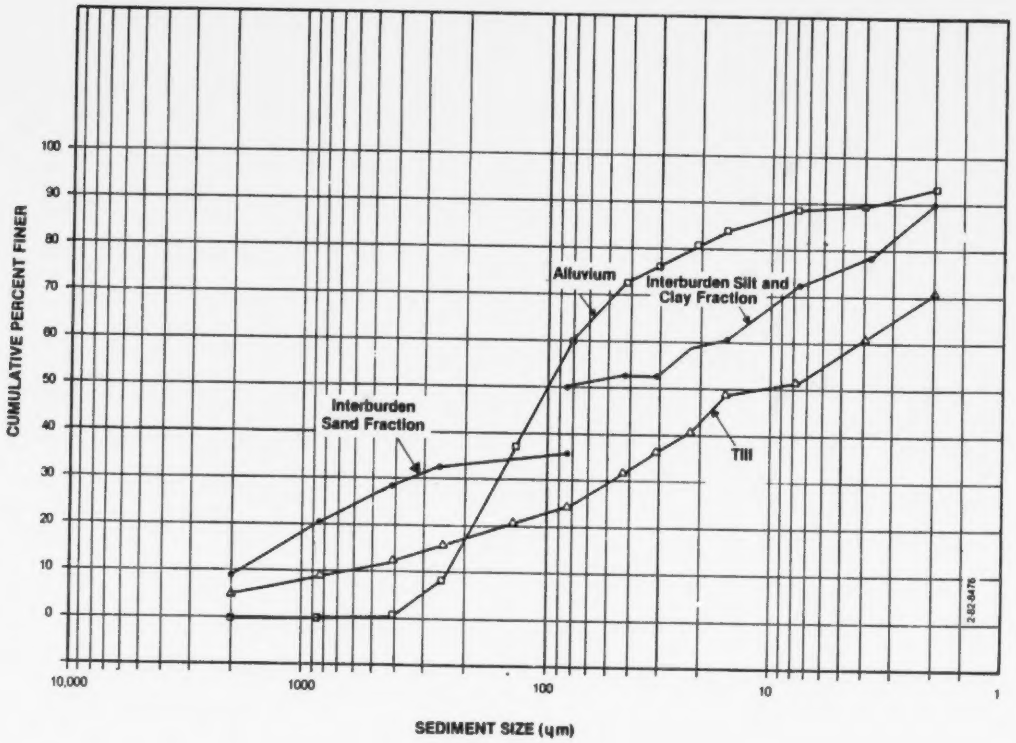
[1] Restir.

TABLE B-7. PIPETTE ANALYSIS OF ALLUVIUM

Diameter (mm)	Withdrawal Depth (cm)	Time	Weight of Beaker (g)	Weight of Beaker + Sample (g)	Weight of Sample (g)	Corrected Weight (−0.060 g Calgon)	X 50 (g)	Cumulative Percent Coarser
0.074	20	20 sec	48.54	49.05	0.51	0.385	19.25	59.7
0.044	20	1 min 45 sec	49.46	49.84	0.38	0.255	12.75	73.3
0.031	10	1 min 45 sec[1]	50.08	50.42	0.34	0.215	10.75	77.5
0.0221	10	3 min 28 sec	49.44	49.75	0.31	0.185	9.25	80.6
0.0156	10	6 min 58 sec	48.17	48.45	0.28	0.155	7.75	83.8
0.0078	10	28 min	49.04	49.27	0.23	0.105	5.25	89.0
0.0039	10	1 hr 52 min	49.92	50.14	0.22	0.095	4.75	90.0
0.0020	10	7 hr 24 min	48.92	49.11	0.19	0.065	3.25	93.2

NOTES: Sand fraction weight = 28.49g
Total sample weight = 47.74g

[1] Restir.



The percentage of material finer than 74 microns for the interburden sample is represented by two data points (36% and 51%). Due to the mixture of clay with consolidated material composing the interburden media, the sand size distribution was determined by dry sieving while the silt and clay fraction was subjected to wet sieving prior to the pipette analysis. The consolidated nature of the interburden resulted in variability in representativeness of the two samples dry sieved and wet sieved at the junction of the sand and silt/clay size fractions.

Figure B-15. Grain Size Distribution Curve for Alluvium, Interburden, and Till.

TABLE B-8. DETAILED DESCRIPTIONS OF GRAIN-SIZE, TEXTURE, AND COMPOSITION OF THE DISPOSAL MEDIA

Disposal Medium	Color	Median Grain Size	Grain Size Name	Sorting	Textural Maturity	Textural Relations
Shale						
Type 1	Tan	Clay size	Clay shale	Very well sorted	Immature	Fissile; sand sized grains of quartz (well rounded) and muscovite (mica).
Type 2	Grey	Clay size	Clay shale	Very well sorted	Immature	Extremely fissile; breaks very easily; very soft.
Type 3	Dark grey	0.05 mm, coarse silt size	Siltstone	Moderatly sorted	Submature	Thin laminae; hematite as grains and masses partially dissolved and filled some pore spaces.
Entire Shale Sample	Light brownish grey	Clay size	—	Very poorly sorted	—	—
Interburden	Dark grey	About 0.0078 mm, very fine silt	Mud-shale	Poorly sorted	Immature	Fissile shale.
Sandstone						
Type 1	White	0.50 mm	Moderately sorted coarse sandstone	Moderately sorted	Submature	Hard - no layering.
Type 2	Dark grey	0.0039 mm	Clay-shale	Poorly sorted	Immature	Fissile - larger grains are predominantly micas.
Type 3	Silver grey	0.105 mm, very fine sand	Moderately sorted very fine sandstone	Moderately sorted	Submature	Packing has occurred, micas appear to be "squashed" by quartz grains.
Entire Sandstone Sample	—	0.203 mm, fine sand	Clayey fine sandstone	Moderately sorted	—	Quartz & mica grains, long axis similarly oriented. Sedimentary structures - laminations. Grains sub-angular to sub-rounded.
Glacial Till	Tan	0.0156 mm, medium silt	Granular mud	Very poorly sorted	Immature	Unconsolidated gravel, sub-rounded; very coarse sand, very angular to rounded; medium sand, sub-angular to sub-rounded.
Alluvium	Tan-brown	0.088 mm, very fine sand	Slightly gravelly silty fine sand	Poorly sorted	Immature	Unconsolidated gravel; very coarse sand, sub-angular to sub-rounded; coarse sand, angular to rounded; medium and fine sand, sub-angular; fines, angular to sub-angular.

NOTE: Textural maturity is based upon the clay content, sorting, and roundness of the grain. Immature sediment contains over 5% terrigenous clay matrix, sand grains usually poorly sorted and angular. The submature stage contains under 5% clay, but sand grains are still poorly sorted and not well rounded.

(Continued)

TABLE B-8. (Continued)

	Gravel Fraction			Sand Fraction			Mud (Silt and Clay) Fraction	
Disposal Medium	Percent	Median Grain Size	Range	Percent	Median Grain Size	Range	Percent	Silt Versus Clay
Shale								
Type 1	0	—	—	2	0.125 mm	0.0625 mm (very fine sand) to 0.25 mm (fine sand)	93	~100% clay
Type 2	0	—	—	0	—	—	100	—
Type 3	0	—	—	5	0.105 mm	0.0625 mm (very fine sand) to 0.25 mm (fine sand)	94	95% silt, 5% clay
Entire Shale Sample	0	—	—	2	0.115 mm	0.0625 mm (very fine sand) to 0.25 mm (fine sand)	95	28.3% silt, 62.5% clay
Interburden	0	—	—	3-5	Fine sand	Medium to very fine sand	95-97	Silt slightly more than clay
Sandstone								
Type 1	0	—	—	100	About 0.50 mm	Very coarse sand to medium sand	0	—
Type 2	0	—	—	5	About 0.105 mm very fine sand	Fine sand to very fine sand	95	85% clay, 10% silt
Type 3	0	—	—	95	0.105 mm very fine sand	Medium sand to very fine sand	5	All silt
Entire Sandstone Sample	0	—	—	67	0.237 mm	Very coarse to very fine sand	23	Mostly clay
Glacial Till	6	3.56 mm, granule	2 to 25 mm, poorly sorted	20	About 0.30 mm, medium sand	0.0625 mm to 2.00 mm, very fine sand to very coarse sand, poorly sorted	75	About half clay
Alluvium	0.1	4 mm	2 to 14 mm, poorly sorted	60	About 0.149 mm, fine sand	0.0625 mm to 2 mm, moderately sorted	40	Silt portion 3 X clay portion

TABLE B-9. DESCRIPTION OF LIMESTONE THIN SECTION

Authigenic Constituents (Matrix)

Sparry Calcite Crystals	
Average Size	0.055 mm
Range:	0.01 to 1.0 mm
Textural Grain Size:	Finely crystalline

Allochemical Constituents (Grains)

Average Grain Size:	0.1 mm
Extreme Range:	0.05 to 2.0 mm
Textural Name:	Very fine calcarenite

Grain Types

1. Fossils (biogenic)

Types:	Foraminifera, burrows, broken shells
Percent of Grains:	60
Average Size:	0.1 mm
Size Ragne	0.5 to 1.0 mm

2. Pellets

Percent of Grains:	38
Average Size:	0.1 mm
Size Range:	0.07 to 0.12 mm

3. Intraclasts

Percent of Grains:	2
Average Size:	1.0 mm
Size Range:	0.1 to 2.0 mm

B.4.1.2 Particle Size Distributon of the Ground Disposal Media

Most of the disposal media were analyzed for average particle size after the samples were ground to the same extent as they were before they were utilized in the laboratory leaching protocol (see Appendix D). Because the fine fraction of the media was initially believed to be the most chemically active material, the particle size analysis was performed on the fraction which was less than 104 microns in diameter using the SediGraph Particle Size Analyzer. The interburden and alluvium samples contained particles too large for size analysis by this method, which indicates that a large fraction of these two samples consisted of particles larger than 104 microns. Results of the average particle size analysis for the other media are given in Table B-10.

TABLE B-10. PARTICLE SIZE PROPERTIES OF GROUND DISPOSAL MEDIA

Disposal Medium	Average Particle Size (E.S.D.[1], μm)
Shale	7.4
Sandstone	8.2
Glacial Till	3.2
Limestone	3.6

[1] E.S.D. = Equivalent Sphere Diameter
[2] ND = Not Determined

The medium having the smallest average particle size, thus providing the largest surface area for reaction, is glacial till. The interburden, alluvium, and shale samples displayed larger surface areas than the sandstone and limestone samples.

B.4.2 Specific Surface Area

The specific surface aras of the ground media ranged from 5.5 m^2/g to 23.8 m^2/g (Table B-11). The specific surface areas of the ground media generally fell into two groups. The limestone, sandstone, and alluvium comprise the lower surface-area group. The shale, interburden, and glacial till constitute the higher surface area group.

TABLE B-11. SPECIFIC SURFACE AREAS OF GROUND DISPOSAL MEDIA

Disposal Medium	Specific Surface Area (m^2/g)
Shale	15.6
Interburden	17.1
Sandstone	8.2
Glacial Till	23.8
Alluvium	10.4
Limestone	5.5

B.4.3 Specific Gravity

The specific gravity measurements of the disposal media are shown in Table B-12. The shale sandstone, glacial till, alluvium, and limestone have very similar densities. The mine interburden is somewhat less dense, probably because of the high percentage of coal fragments.

TABLE B-12. SPECIFIC GRAVITIES OF DISPOSAL MEDIA

Disposal Medium	Specific Gravity
Shale	2.72
Interburden	2.25
Sandstone	2.75
Glacial Till	2.77
Alluvium	2.76
Limestone	2.81

B.4.4 Particle Surface Characteristics

Observations of scanning electron photomicrographs, which were taken of ground disposal media, show definite similarities among certain media. The interburden, sandstone, and shale samples exhibit surface similarities at low magnification (Figures B-16a, B-17a, and B-18a). Small crystals appear to be deposited on larger irregularly shaped flakes (normally observed for various clay minerals). While the shale and sandstone media appear flatter with laterally associated stacks, the larger interburden particles are composed of shorter flakes with greater vertical dimension (Figures B-16b, B-17b, and B-18b). The sandstone sample appears to have the least particle size variation among these three media samples.

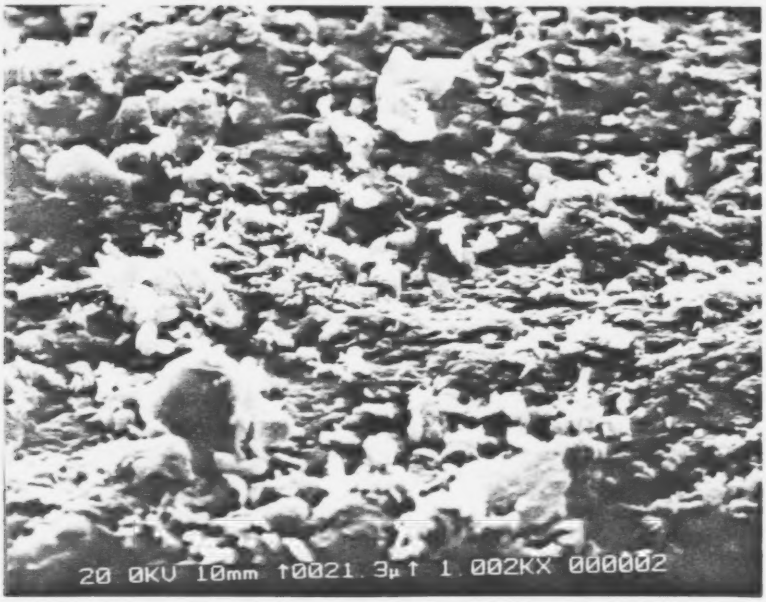
The disposal medium having the most crystalline surfaces is the limestone. Small well-defined crystals appear to cover the surface, as seen at low magnification in Figure B-19a. At higher magnification (Figure B-19b), largely platey materials can be ovserved in the background.

The glacial till sample is similar to the limestone medium, but the particles are somewhat larger. The surface heterogeneity is slightly reduced in this disposal medium, compared to the limestone (Figure B-20).

The least crystalline surface is observed for the alluvium medium. This medium contains large clay-like plates that are almost entirely in two orientations, as shown in Figure B-21. These ill-defined plates occur over the entire surface with great uniformity.

Photomicrographs were also taken of shale and sandstone residues after protocol Step 1 leaching with deionized water. After the Step 1 leachate was removed for analysis, additional deionized water was added to the solids and the leaching process was repeated for an additional seven days as in protocol Step 2. At the end of the seventh repetition, the solid residue was retained for analysis. A total of 32 leachate and four solid samples were generated by this experiment. Figures B-22 and B-23 show electron micrographs of these leached residues. The sandstone and shale after leaching show no visual differences from the unleached media.

The leachate produced from leaching shale and sandstone was used to leach the Alliance AFBC waste. Duplicate portions of the waste were initially leached for seven days with Step 1 type leachates from both shale and sandstone. After the seven-day equilibration period, the liquid was removed for analysis and the solids were carried forward into secondary leaching using additional Step 1 type leachates from the disposal media. The secondary leaching (Step 2 type) process was repeated seven times. At the end of the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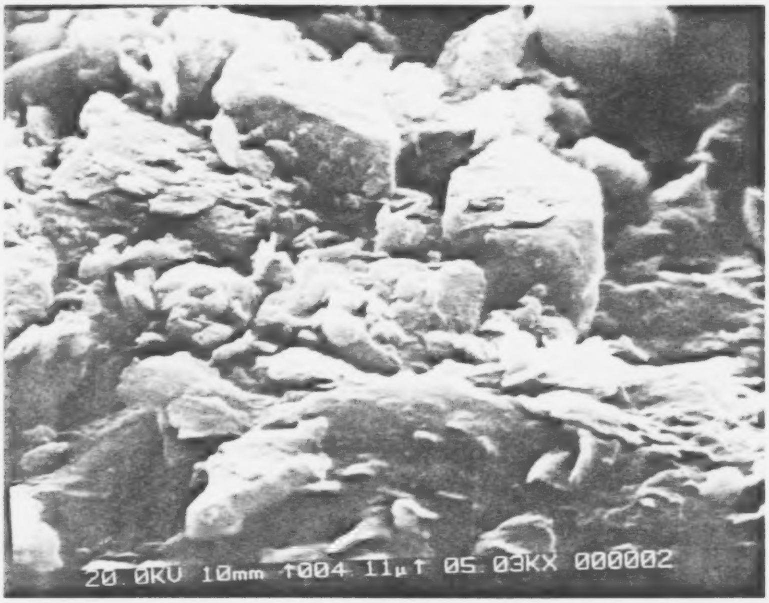
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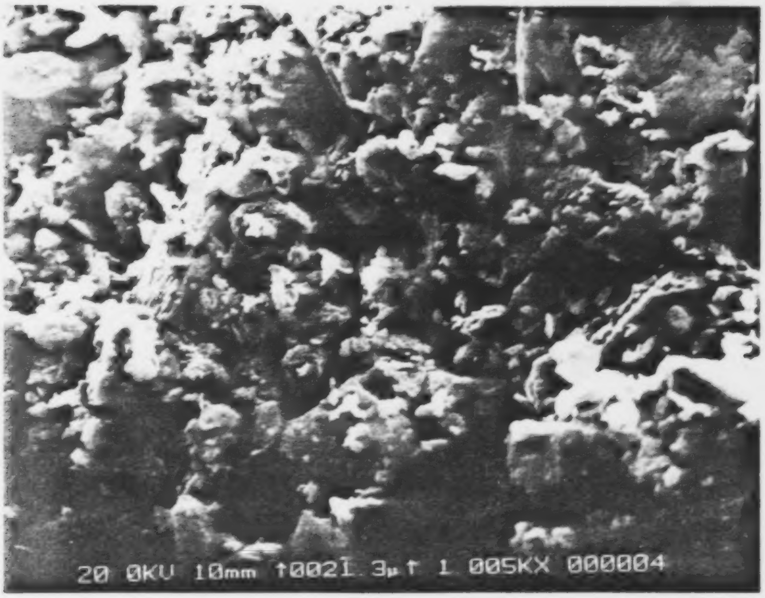
b. Magnification = 5000X

Figure B-16. Scanning Electron Micrographs of Mine Interburden.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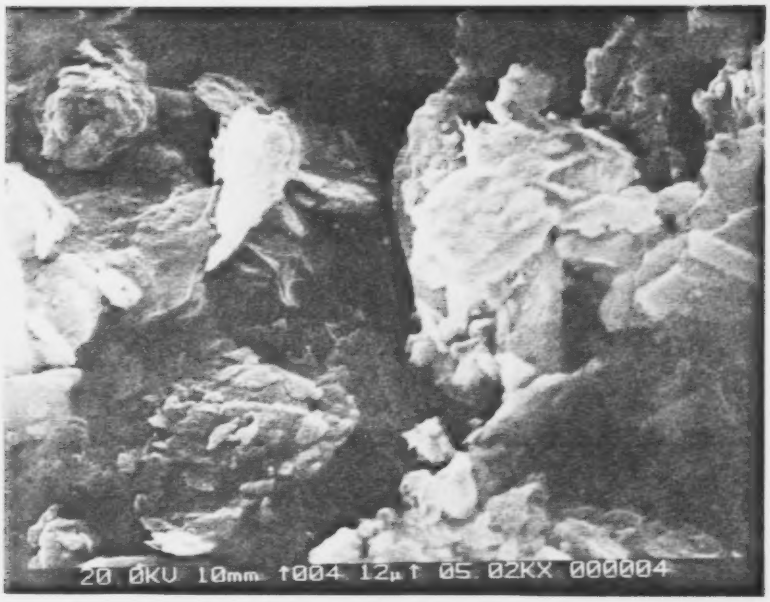
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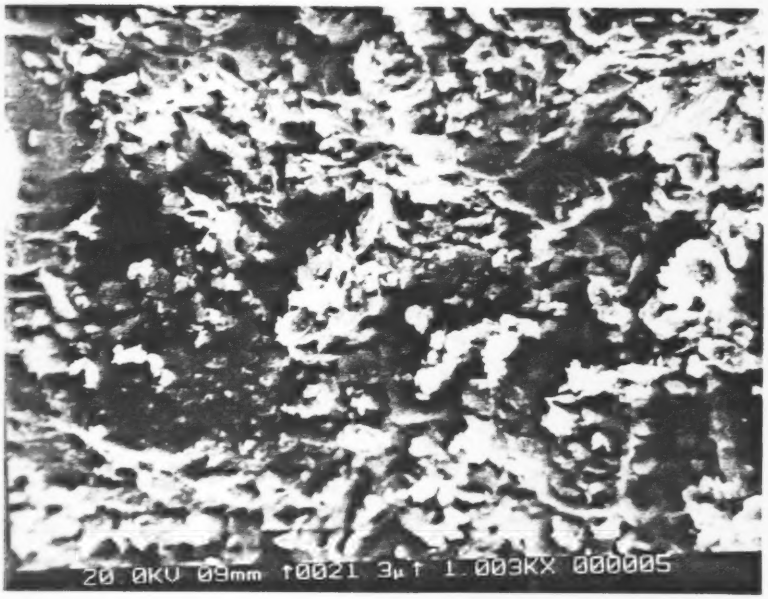
b. Magnification = 5000X

Figure B-17. Scanning Electron Micrographs of Sandstone.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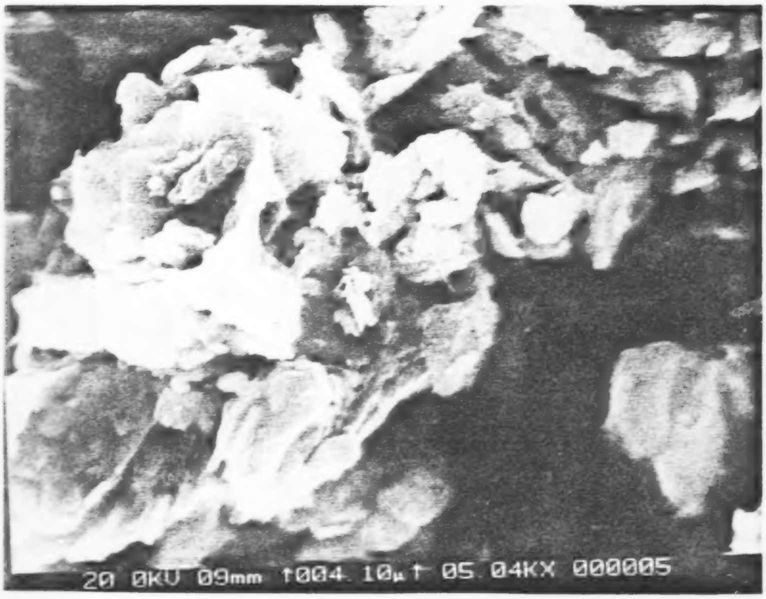
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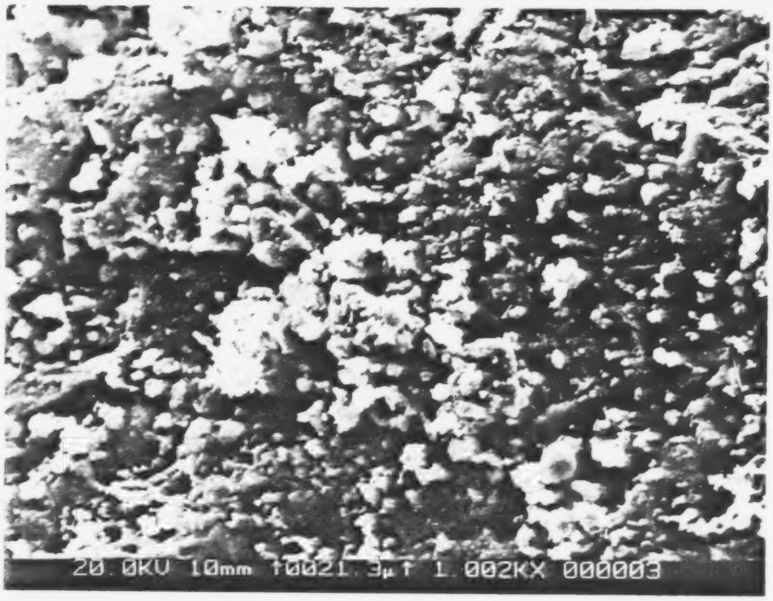
b. Magnification = 5000X

Figure B-18. Scanning Electron Micrographs of Shale.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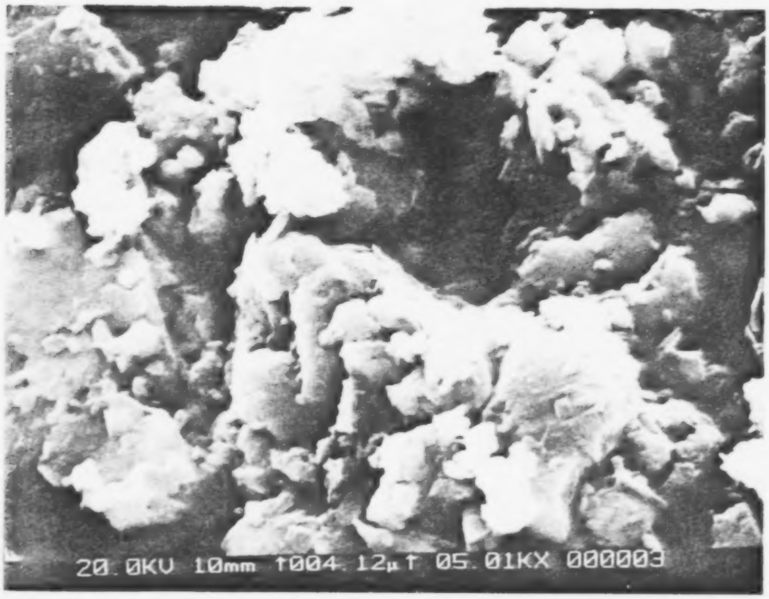
a. Magnification = 1000X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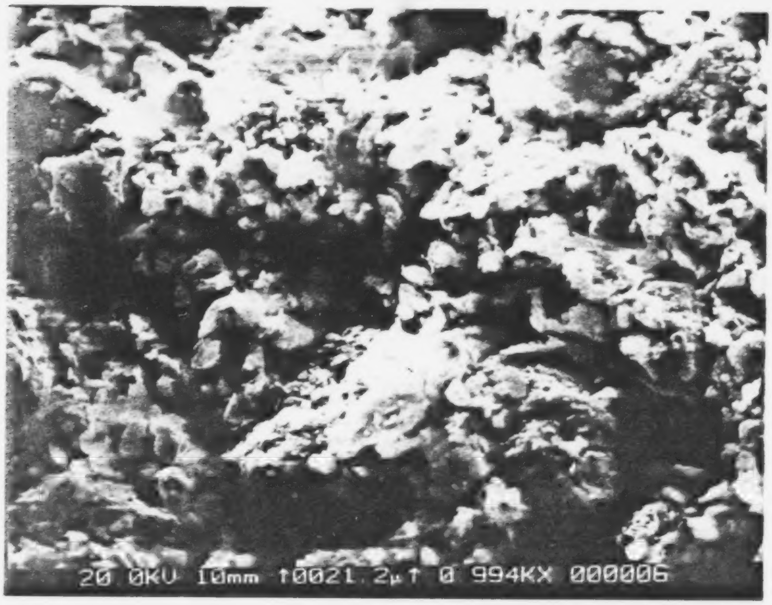
b. Magnification = 5000X

Figure B-19. Scanning Electron Micrographs of Limestone.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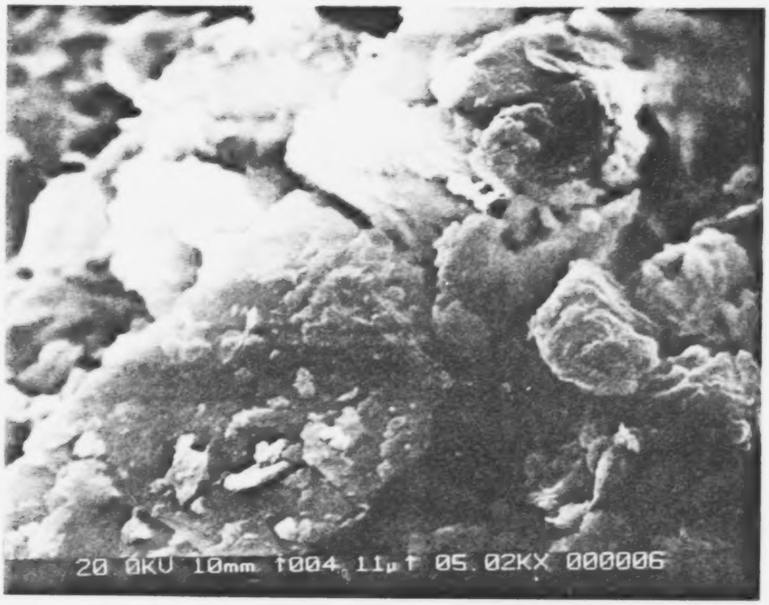
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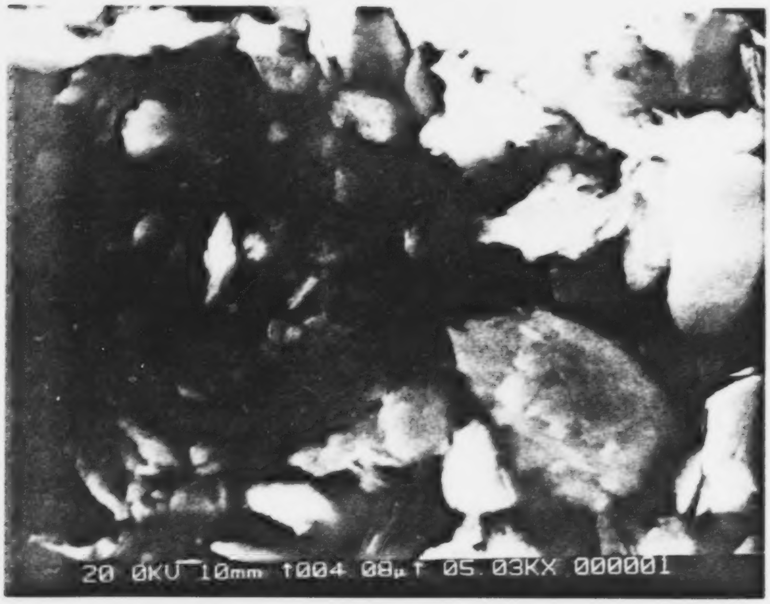
Figure B-20. Scanning Electron Micrographs of Glacial Till.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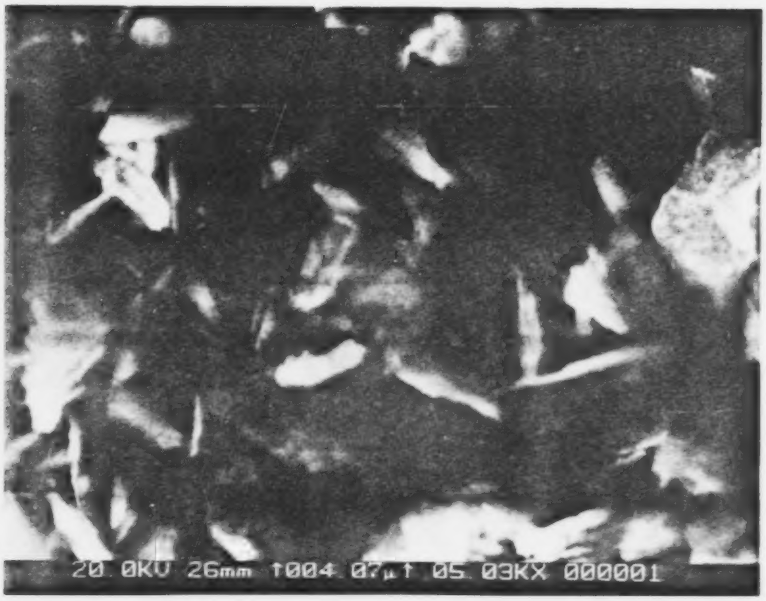
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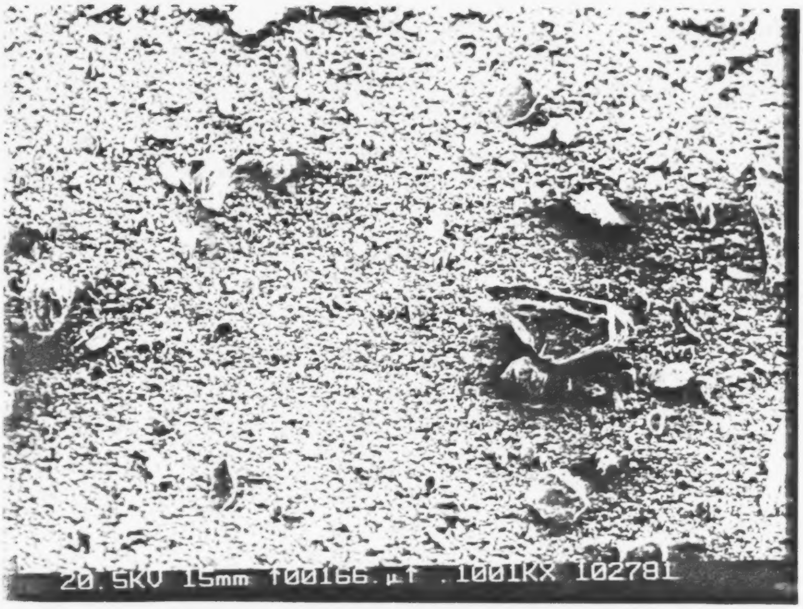
b. Magnification = 5000X

Figure B-21. Scanning Electron Micrographs of Alluvium.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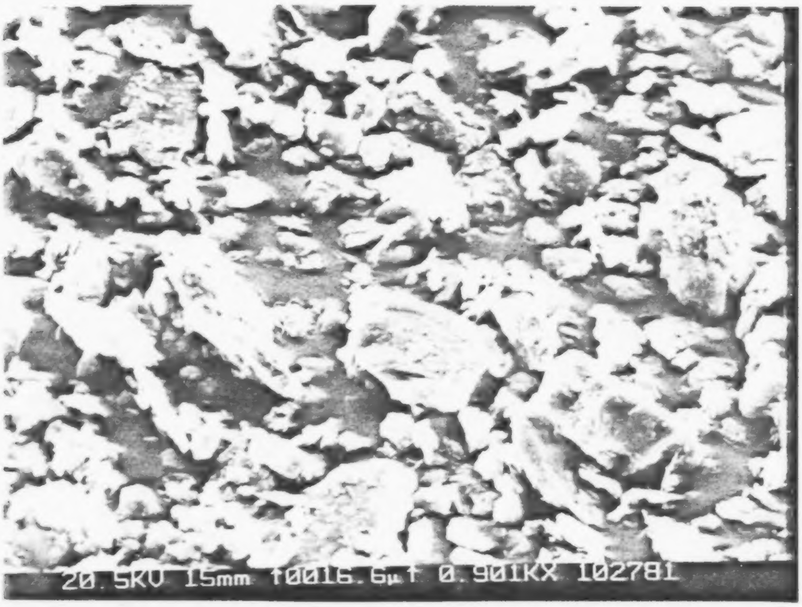
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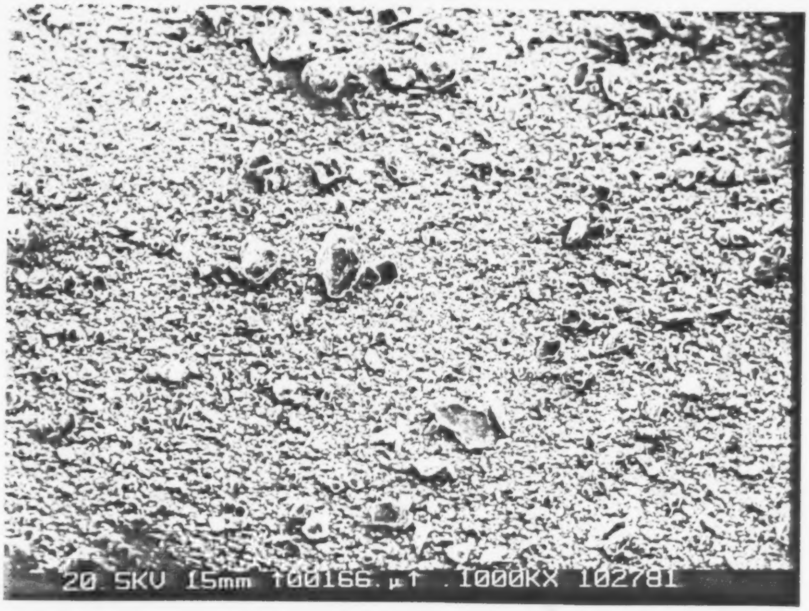
b. Magnification = 1000X

Figure B-22. Scanning Electron Photomicrographs of Sandstone After Repeated Leaching with Water.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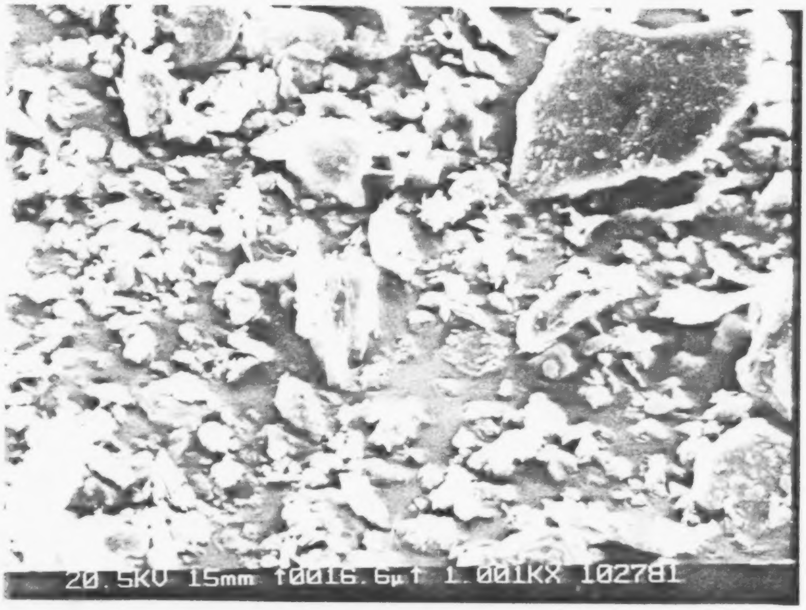

20.5KV 15mm †0016.6μ† 1.001KX 102781

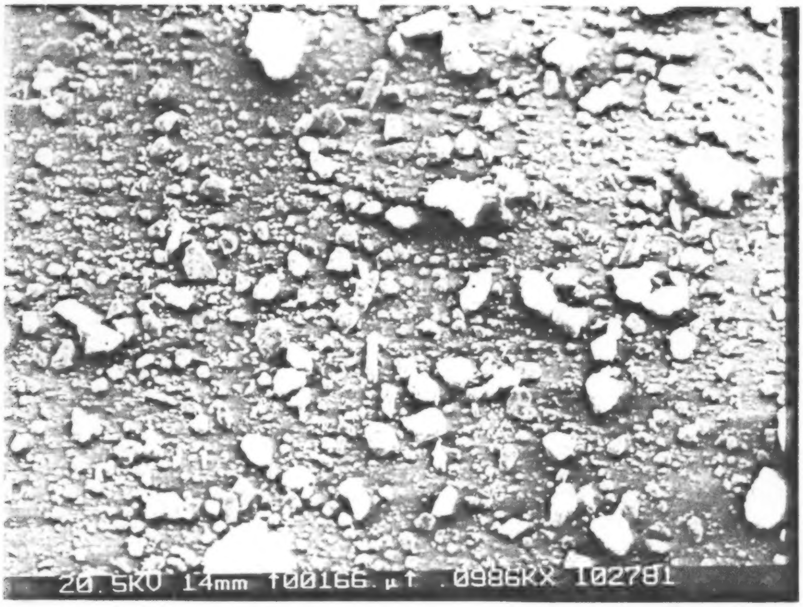
b. Magnification = 1000X

Figure B-23. Scanning Electron Photomicrographs of Shale After Repeated Leaching with Water.

seventh repetition, the solid residue was also retained for analysis. This experiment generated a total of 32 leachates and four solid samples for analysis. Figures B-24 and B-25 show the waste residues. The waste leached with the sandstone and shale liquor show heavy crystallization of small particles on the surfaces of large particles.

B.5 References

B-1. Folk, R.L., 1974, Petrology of Sedimentary Rocks, Hemphill Publishing Co.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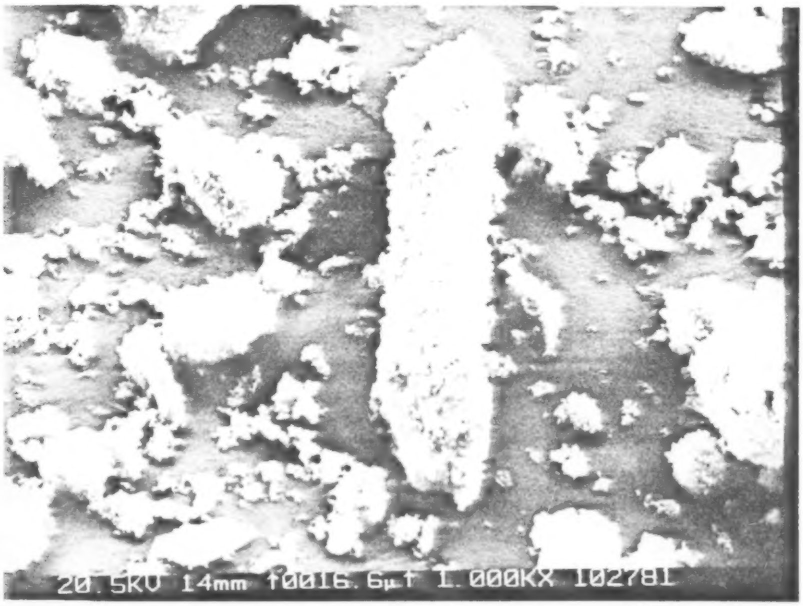
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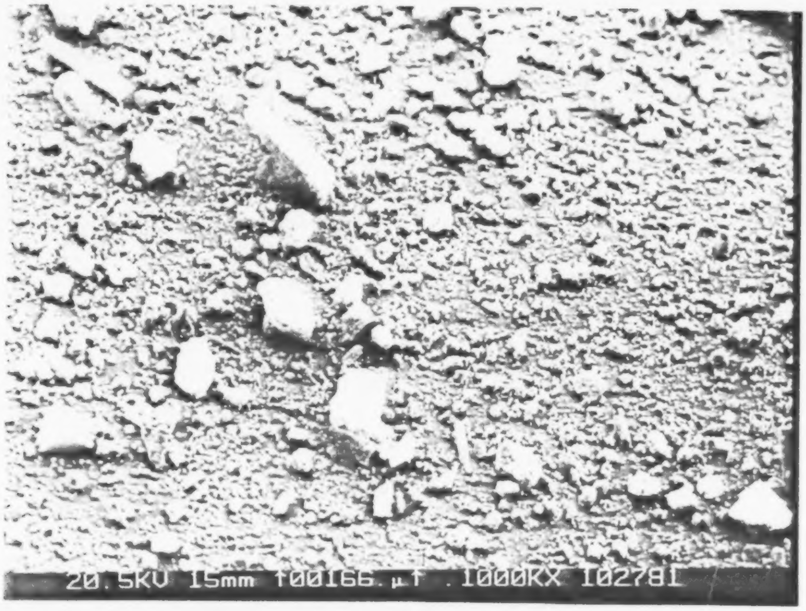
b. Magnification = 1000X

Figure B-24. Scanning Electron Photomicrographs of Alliance AFBC Waste After Repeated Leaching with Sandstone Leachate.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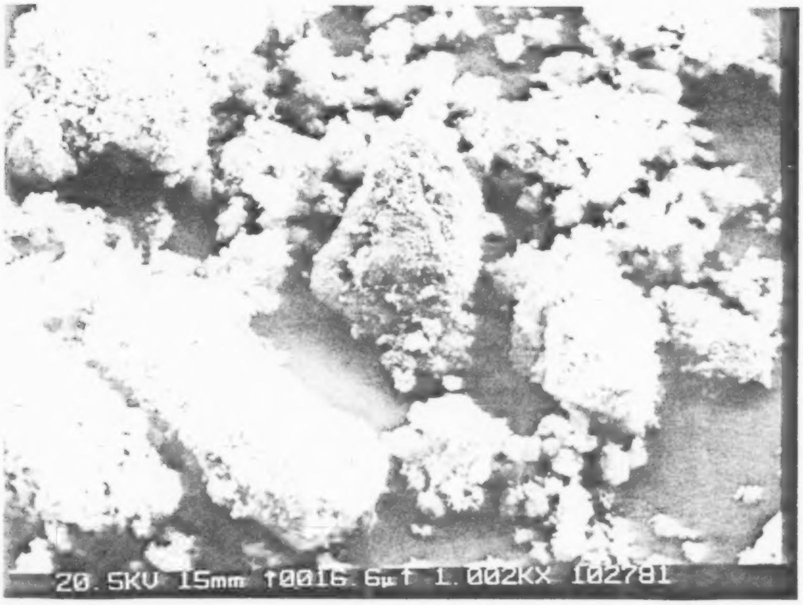
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b. Magnification = 1000X

Figure B-25. Scanning Electron Photomicrographs of Alliance AFBC Waste After Repeated Leaching with Shale Leachate.

Appendix C

SOLIDS COMPOSITION OF
FBC SOLID WASTES AND DISPOSAL MEDIA

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Appendix C

FBC SOLID WASTE AND DISPOSAL MEDIA WHOLE-SAMPLE COMPOSITION

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C.1 Overview

The solids compositions of both the FBC solid waste samples and the disposal media samples were determined by several methods. The mineral composition was determined by X-ray diffraction analysis and binocular microscope examination. The presence and distribution of certain elements within the particles were determined by X-ray fluorescence and electron microprobe analysis. The elemental compositions were obtained by total digestion of the samples and chemical analysis of the digest solution. Standard ultimate and proximate analyses were also performed on the wastes and disposal media.

X-ray powder diffraction investigation of the Exxon PFBC waste before leaching showed that the major crystalline components were anhydrite ($CaSO_4$), periclase (MgO) and quartz (SiO_2). X-ray powder diffraction patterns for the PFBC waste after laboratory leaching (protocol Steps 1 and 2) showed gypsum ($CaSO_4 \cdot 2H_2O$), brucite ($Mg(OH)_2$), and quartz. X-ray powder diffraction patterns of leached PFBC wastes removed from three field cells (Cells 2, 3, and 5) were very similar. These wastes contained ettringite ($Ca_{12}Al_3(SO_4,SiO_3,CO_3)_6(OH)_{11} \cdot 30H_2O$) gypsum, calcite ($CaCO_3$), brucite, and quartz. No portlandite ($Ca(OH)_2$) or hematite (Fe_2O_3) were present.

X-ray powder diffraction patterns of the Alliance AFBC waste before leaching showed anhydrite, lime (CaO), quartz, calcite, portlandite, and hematite. A waste "representativeness" test involving X-ray diffraction of five randomly selected samples of unleached Alliance AFBC waste showed that the samples were very similar, indicating that each sample contained approximately the same mineral ratios. X-ray powder diffraction patterns of the Alliance AFBC waste after leaching showed that gypsum, portlandite, quartz, ettringite, and calcite were present. X-ray powder diffraction patterns of leached Alliance AFBC wastes removed from three field cells (Cells 13, 14, and

17) were similar and contained primarily portlandite, gypsum, and calcite with smaller amounts of ettringite and hematite. The waste in Cell 13 appeared to contain slightly more portlandite while the waste from Cell 17 contained slightly less gypsum than the other two cells. The residues from repetitive leaching of Alliance AFBC waste with leachate from shale and sandstone were also analyzed by X-ray diffraction. This analysis showed that these residues contained ettringite, gypsum, portlandite, anhydrite, hematite, lime, quartz, and calcite.

X-ray powder diffraction patterns of unleached Georgetown AFBC waste showed the same crystalline components as the Alliance AFBC waste, except in different quantities. The Georgetown AFBC waste contained more portlandite and quartz and much more lime. It also contained less gypsum, calcite, and hematite than than the Alliance AFBC waste. X-ray powder diffraction patterns of ground and unground Georgetown AFBC waste after leaching were similar and contained etrringite, gypsum, portlandite, anhydrite, hematite, lime, and calcite and quartz.

The X-ray fluorescence analysis showed that the major difference between Exxon PFBC and Alliance AFBC waste composition was a higher concentration of magnesium in the PFBC waste owing to differences in the sorbent. X-ray fluorescence indicated that both PFBC and Alliance AFBC wastes contained aluminum, silicon, sulfur, potassium, calcium, and iron. X-ray fluorescence of the bulk samples of Alliance AFBC waste residues that had been repeatedly leached with leachate from shale and sandstone were very similar, with major quantities of calcium and minor amounts of aluminum, silicon, sulfur, and iron. X-ray fluorescence analysis of bulk samples of ground and unground Georgetown AFBC waste after leaching yielded similar results; the samples contained aluminum, silicon, sulfur, potassium, calcium, and iron. The leached sample appeared to contain slightly less aluminum, iron, and silicon and slightly more potassium than the unleached sample based upon the relative intensities of characteristic elemental fluorescence. X-ray fluorescence analysis of five randomly selected samples of unleached Alliance AFBC waste indicated the presence of aluminum, silicon, sulfur, potassium, calcium, and iron. Only slight variations in the concentrations of potassium and iron were apparent.

X-ray powder diffraction patterns for the limestone and glacial till samples showed that the major components were quartz, calcite, and dolomite. The crystalline component determined for the alluvium was quartz, and there was some evidence of the minerals muscovite and albite. X-ray diffraction scans of the shale, sandstone and interburden indicated the presence of quartz and several naturally occurring clay minerals. X-ray powder diffraction of shale and sandstone that had been repetitively leached with deionized water showed the presence of quartz, kaolinite, illite, muscovite, hematite, and possibly chlorite and phlogopite. The leached sandstone contained slightly more quartz than the shale sample.

X-ray fluorescence of the bulk samples of repetitively leached (with deionized water) shale and sandstone showed very similar results, with major quantities of aluminum and silicon and with less calcium, titanium, and iron.

C.2 Methods

The solids composition of the FBC wastes was determined first in a fresh, unleached condition. The composition was determined again after the wastes had been leached according to the batch equilibration protocol used in the laboratory leaching studies. The objective was to determine the extent of alteration resulting from the leaching of the wastes. Likewise, the composition of each of the disposal media was determined in the fresh state prior to exposure to waste leachate and again after exposure to the leachate in the laboratory protocol.

The composition of the FBC waste was determined by X-ray diffraction, X-ray fluorescence, sample digestion and analysis of the digest solution, and ultimate and proximate analysis by ASTM methods. The composition of the disposal media was determined by several methods: 1) microscope examination (including both binocular microscope examination of unconsolidated materials and polarizing microscope examination of thin sections of consolidated material); 2) X-ray diffraction analysis for mineralogical determinations; 3) sample digestion and chemical analysis of the digest solution for determination of chemical composition of the solids; and 4) ultimate and proximate analysis.

C.2.1 X-Ray Diffraction

X-ray diffraction analysis of the wastes and disposal media was performed to identify the crystalline phases present. Polycrystalline powder patterns were obtained for the individual FBC waste streams and for composited FBC waste before and after leaching. Similar powder patterns were prepared from the disposal media before and after exposure to the FBC leachate.

In the method used, a powder sample composed of an aggregate of a large number of tiny crystallites was prepared so that the crystallites were in random orientation. X-radiation emitted from a copper (K_α) source was directed upon the randomly oriented flat sample. A complete diffraction scan from 10° to 90° was recorded for each specimen. As the specimen was irradiated by the incident X-radiation, each set of crystal planes in the various crystallites produced a diffracted beam, which was then detected by a scintillation counter. The signal was recorded as a pattern on chart paper. The patterns, which were a series of X-ray intensity peaks, were taken using a Siemens X-Ray Powder Diffractometer. The scan was recorded at a rate of 1 degree per minute. Interplanar d-spacings were calculated from the X-ray intensity peaks using Bragg's Law. The indexed d-spacings for various components were identified by a hand search of the Hanawalt Index Powder Diffraction File and by comparing the experimentally obtained spacings with those from known pure crystalline compounds.

In general, only crystalline compounds that are present in major proportions (at least five to 10 percent) can be identified by X-ray diffraction. The limits of detectability are strongly dependent on the intrinsic intensity of the diffraction pattern of a crystalline compound and the amount and type of other crystalline species present.

The powder diffraction technique used yields qualitative rather than quantitative information, but some semi-quantitative information is also available. For a given crystalline species, the intensity of the pattern will increase with an increasing amount present in the sample. However, if two species are present, the one with the more intense pattern is not necessarily present in higher proportion, since parameters other than amount may influence the intensity of an x-ray diffraction peak.

C.2.2 X-Ray Fluorescence

X-ray fluorescence scans (XRF) were taken of the Exxon PFBC and Alliance AFBC wastes before and after leaching in order to determine the impact of leaching on concentrations of key elements present on the surface of the wastes. The electron beam in the SEM displaces an inner orbital (L or K shell) electron, and the subsequent collapse of a high energy electron into the "hole" releases a photon of high energy in the form of X-radiation. Elemental composition of samples placed in the SEM can be obtained by analyzing information provided by the fluorescent radiation. This information can be displayed as peaks on a curve depicting counts as a function of energy. The peak position (energy) is used to identify major elements (with atomic number 11 or above) present in the sample. Peak height can provide semi-quantitative information on the amount of each element in the sample.

The XRF spectra are presented in plots of counts as a function of energy. The counts, which are related under certain conditions to the amount of each element in the sample, are the result of line radiations reflected according to the Bragg condition at the detector where the energy of the X-ray quanta is converted into electrical impulses. The energy (KeV) is determined by dividing the wavelength of each line (first order) or absorption edge into the value for hv, where h is Planck's constant and v is the frequency of radiation. This process was done automatically within the scanning electron microscope and the XRF spectrum was projected onto a cathode ray tube. The elements used as sample coating (gold and palladium) were removed by a multichannel analyzer and spectral stripping using background intensities from blank sample coating. A printer was used to produce a hard copy of the resultant spectra.

The intensities of fluorescent emission presented in this section were not corrected for matrix effects. The intensity of a given line can be enhanced if a matrix element absorbs primary radiation, and then, by fluorescence, emits radiation which, in turn, is absorbed by a sample element and causes the sample to fluoresce more strongly. The observed relative intensities are dependent upon several experimental parameters including energy of the electrons causing the excitation, self-absorption within the sample, and wavelength-dependent response or efficiency of the crystal and the detector. Without applying complicated correction programs, these XRF data are primarily qualitative in nature. However, approximate semiquantitative comparisons could be made since all instrumental operating conditions were held constant during the course of this analysis.

C.2.3 Electron Microprobe Analysis

The electron microprobe analysis was accomplished by varying the accelerating current of the electron beam in the scanning electron microscope so that two levels within the sample were analyzed. An X-ray fluorescence scan was performed to achieve elemental analysis of the two levels, and concentrations of elements seen at these two levels were compared. Such information can be useful in determining distribution of a given element between the surfaces and the interiors of particles.

C.2.4 Solid Sample Digestion and Analysis

Composite samples of the Exxon PFBC and Alliance AFBC wastes, components of the PFBC waste stream, and leached samples of Exxon PFBC and Alliance AFBC wastes from Steps 2 and 5 of the laboratory protocol were digested, and the chemical compositions of the digest solutions were determined. Various digestion and extraction methods were used to free the species of interest from the individual samples matrices. These methods included the following:

- Lithium metaborate fusion for subsequent determination of major metallic constituents;

- Perchloric acid digestion for determination of minor and trace metallic constituents;

- Sodium carbonate fusion for determination of boron and fluoride; and

- Nitric acid extraction for determination of sulfate and chloride.

The step-by-step procedures for these methods are given in Tables C-1 to C-4. The parameters analyzed in the digest solution and the methods of analysis are shown in Table C-5.

C.2.5 Proximate and Ultimate Analysis

The FBC solids and disposal media were further characterized by ultimate and proximate analyses. The analyses were conducted by a subcontractor, Commercial Testing Engineering Company. The following parameters were determined:

Proximate Analysis
% Moisture
% Ash
% Volatile Matter
% Fixed Carbon (by difference)

Ultimate Analysis
% Carbon
% Hydrogen
% Nitrogen
% Sulfur
% Oxygen (by difference)

Heating value (Btu/lb) is usually reported with results of the proximate analysis.

TABLE C-1. PROCEDURE FOR LITHIUM METABORATE FUSION

Sample Type: Silicates, Ash
0.1 g of solid sample into platinum or graphite crucible
0.6 g $LiBO_2$
Mix
Fuse at 1050°C for 15 minutes
Remove from heat and immediately pour the molten sample into 50 mL deionized water
5 mL HCl
Heat at 50°C for three hours
Cool
Dilute to 250 mL

TABLE C-2. PROCEDURE FOR PERCHLORIC ACID DIGESTION

Sample Type: Solids, High Silica Content

0.5 g of solid into 100 mL Teflon beaker (carbonaceous solids should be ashed before digestion)

25 mL HNO_3

Cover with Teflon watch glass

Heat at 50°C for 10 hours

Cool

10 mL HNO_3

5 mL HCl

5 mL HF

Cover, heat at 50°C for 10 hours

Boil for 1 hour

Cool

5 mL $HClO_4$

Heat uncovered until white fumes of $HClO_4$ appear

If solution is still black, repeat HNO_3 and $HClO_4$ treatment, add 10 mL 30% H_2O_2, heat

Cool

Wash Down the side of beaker with ~2 mL deionized water

Evaporate to dryness

*** CAUTION: The sample is very explosive at this time

Heat until sample turns black or brown

Cool

2 mL HNO_3 or HCl

50 mL deionized water

Warm until solution becomes clear

Cool

Dilute to 100 mL

Note: Do only in perchloric acid hood.

TABLE C-3. PROCEDURE FOR SODIUM CARBONATE FUSION

Sample Type: Silicates

0.5 g of sample into platinum crucible

1.5 g Na_2CO_3

Mix

Sprinkle 0.5 g Na_2CO_3 on top of mixture

Place crucible in cold muffle furnace and raise temperature slowly to 600°C

Leave crucible in furnace at 600°C for at least 6 hours

Cool

Fuse over flame until molten

Cool

Add dilute sulfuric acid to dissolve melt, being careful not to lose any sample due to effervescence

Dilute to 100 mL

TABLE C-4. PROCEDURE FOR NITRIC ACID EXTRACTION

Sample Type: Sulfate and Chloride

0.5 g of sample into 60 mL bottle

50 mL of 0.1N nitric acid

Cap bottle and shake overnight

Allow solids to settle

Filter supernatant liquid in glass fiber filter (which was prewashed with nitric acid and rinsed with deionized water)

TABLE C-5. PARAMETERS AND METHODS OF CHEMICAL ANALYSIS FOR SOLID SAMPLES OF FBC SOLID WASTES

Element/	Analysis Technique					
Species	ICAPES[1]	Furnace AAS[2]	Flame AAS[3]	SIE[4]	T[5]	SP[6]
Ag		X				
Al	X					
B	X					
Ba	X					
Be	X					
Ca	X					
Cd		X				
Cl						X
Co	X					
Cr	X					
Cu	X					
F				X		
Fe	X					
K	X					
Li			X			
Mg	X					
Mn	X					
Mo	X					
Na	X					
Ni	X					
Si	X					
SO_4					X	
Sr	X					
Ti	X					
V	X					
Zn	X					

[1] Inductively Coupled Argon Plasma Emission Spectrosocpy

[2] Graphite Furnace Atomic Absorption

[3] Flame Atomic Absorption

[4] Selective Ion Electrode

[5] Turbidimetry

[6] Spectrophotometry

C.3 Whole-Sample Composition of FBC Solid Wastes

As noted the composition of FBC solid waste samples was determined by X-ray diffraction, X-ray fluorescence, electron microprobe, and sample digestion and chemical analysis.

C.3.1 X-Ray Diffraction Analysis

X-ray diffraction analysis provides valuable information on the composition of the crystalline phases present in the FBC waste. However, no information is provided on the noncrystalline (amorphous) phases in the waste. The relative abundance of the crystalline and amorphous components of the wastes is not known.

C.3.1.1 Preliminary X-Ray Analysis of IERL-RTP FBC Wastes

During the initial phases of the program, polycrystalline X-ray diffraction studies were carried out on samples of separate waste streams from the FBC unit at the EPA Industrial Environmental Research Laboratory (Research Triangle Park). There was concern about the availability of AFBC-with-carbon-burnup-cell wastes at the time, and AFBC-with-CBC was still one of the technology frontrunners. The purpose of the investigation of the IERL FBC waste was to make a preliminary assessment of the effect of the higher temperature of a CBC unit on the crystallinity of the FBC waste.

X-ray data were obtained from samples of bed draw and primary cyclone wastes. The data were obtained on samples from two operating temperatures of the IERL FBC unit, one at 840°C (1550°F) to represent conditions without CBC operation and one at 1055°C (1930°F) to represent conditions with CBC operations. A summary of the data is presented in Table C-6. These data indicate additional heating had very little effect on the bed draw samples from the IERL-RTP unit, but there was a pronounced effect on the crystallinity of the fly ash sample collected from the primary cyclone. In the fly ash samples, the calcium sulfate and calcium oxide phases are apparently unaffected by changing bed temperature from 840°C to 1055°C. However, the calcite ($CaCO_3$),

TABLE C-6. X-RAY POWDER DIFFRACTION ANALYSIS OF FBC SAMPLES FROM IERL-RTP UNIT

Primary Cyclone Samples (Diffraction Peaks)				Bed Draw Samples (Diffraction Peaks)			
840°C Sample		1055°C Sample		840°C Sample		1055°C Sample	
d-Spacing (Å)	Crystalline Component	d-Spacing (Å)	Crystalline Component	d-Spacing (Å)	Crystalline Component	d-Spacing (Å)	Crystalline Component
4.94	$Ca(OH)_2$						
4.88	Fe_3O_4						
4.26	α-SiO_2						
4.23	unknown						
3.83	$CaCO_3$						
3.48	$CaSO_4$	3.47	$CaSO_4$	3.48	$CaSO_4$	3.47	$CaSO_4$
3.34	α-SiO_2	3.33	α-SiO_2				
3.02	$CaCO_3$						
2.84	$CaSO_4$	2.84	$CaSO_4$	2.84	$CaSO_4$	2.83	$CaSO_4$
2.77	CaO	2.77	CaO	2.77	CaO	2.76	CaO
2.69	α-Fe_2O_3						
2.63	$Ca(OH)_2$			2.63	$Ca(OH)_2$	2.62	$Ca(OH)_2$
2.51	α-Fe_2O_3	2.51	α-Fe_2O_3				
2.40	CaO	2.40	CaO	2.39	CaO	2.39	CaO
2.32	$CaSO_4$			2.32	$CaSO_4$	2.32	$CaSO_4$
2.28	α-SiO_2						
2.20	α-Fe_2O_3			2.20	α-Fe_2O_3		
1.918	$Ca(OH)_2$						
1.866	$CaSO_4$			1.864	$CaSO_4$	1.862	$CaSO_4$
1.744	$CaSO_4$					1.745	$CaSO_4$
1.694	α-Fe_2O_3			1.696	α-Fe_2O_3	1.694	α-Fe_2O_3
1.486	α-Fe_2O_3						
1.481	Fe_3O_4						
1.448	α-Fe_2O_3						

magnetite (Fe_3O_4), quartz (SiO_2), hematite (Fe_2O_3), and portlandite ($Ca(OH)_2$) peaks identified in the 840°C sample were either completely absent in 1055°C sample or were much lower in intensity, indicating a loss of crystallinity.

C.3.1.2 X-Ray Analysis of Exxon PFBC Waste

Samples of both unleached and leached Exxon PFBC waste were subjected to X-ray diffraction analysis. Both of these samples were composite waste containing two parts bed draw, one part Cyclone No. 2, and 0.1 part Cyclone No. 3 waste. The results for the unleached and leached waste are shown in Table C-7. The major crystalline components in the unleached waste were anhydrite ($CaSO_4$), periclase (MgO), and quartz.

The predominant components of the mixed PFBC waste after leaching by Step 2 (seven repetitions) of the laboratory protocol were gypsum ($CaSO_4 \cdot 2H_2O$), brucite ($Mg(OH)_2$), quartz, and calcite. Gypsum and portlandite are the products of chemical reactions between anhydrite and water and between lime (CaO) and water.

As described in Appendix E, core samples were obtained from the field cells at the conclusion of the field program. In the leached waste removed from cells 2, 3, and 5, the crystalline components were identified as ettringite ($Ca_{12}Al_3(SO_4,SiO_3,CO_3)_6(OH)_{12} \cdot 30H_2O$), gypsum, brucite, calcite, and quartz (Table C-8). These are the same components as are present in the leached laboratory waste with the exception of ettringite. The fact that ettringite formed in the field cell waste, but not in the waste leached in the laboratory, probably results from different trends in the leachable sulfate. If sulfate is the controlling species in solution, this formation of ettringite in the field cell and not in the laboratory batch leaching could be important in the leachate chemistry.

X-ray powder diffraction analysis was also performed on components of the Exxon PFBC waste stream. The materials from two runs of Cyclone No. 2 (runs 79 and 80) were found to be composed of major quantities of anhydrite and quartz. These samples also contained some hematite and magnetite. Dolomite

TABLE C-7. INTERPRETATION OF X-RAY POWDER DIFFRACTION PATTERNS OF EXXON PFBC MIXED WASTE BEFORE AND AFTER LABORATORY PROTOCOL LEACHING

Before Leaching		After Leaching	
d-Spacing (Å)	Crystalline Component	d-Spacing (Å)	Crystalline Component
4.924	portlandite	7.550	gypsum
4.247	quartz	4.740	brucite
3.847	anhydrite	4.230	gypsum, quartz
3.477	anhydrite	3.767	–
3.336	quartz	3.324	quartz
3.118	anhydrite	3.046	gypsum, calcite
3.025	–	2.864	gypsum
2.838	anhydrite	2.778	gypsum
2.786	anhydrite	2.680	gypsum
2.688	hematite	2.590	gypsum
2.620	portlandite	2.520	calcite
2.513	hematite	2.495	gypsum
2.459	anhydrite, quartz	2.458	quartz
		2.447	gypsum
2.389	lime	2.371	brucite
2.324	anhydrite	2.400	gypsum
2.282	quartz	2.284	quartz
2.204	anhydrite	2.214	gypsum, calcite
2.179	anhydrite	2.134	gypsum, quartz
2.101	periclase	2.101	calcite
2.086	anhydrite	2.083	–
2.030	–	2.069	gypsum
1.995	anhydrite	2.030	–
1.938	anhydrite	1.987	gypsum
1.867	anhydrite	1.897	gypsum
1.852	anhydrite	1.878	gypsum
1.838	hematite	1.864	gypsum
1.817	quartz	1.817	quartz
1.744	anhydrite	1.806	gypsum
1.697	lime, hematite	1.796	brucite
1.646	anhydrite	1.779	gypsum
1.564	anhydrite	1.663	gypsum
1.487	periclase, anhydrite	1.620	gypsum
		1.584	gypsum
		1.577	brucite
		1.529	gypsum

TABLE C-8. INTERPRETATION OF X-RAY POWDER DIFFRACTION PATTERN OF EXXON PFBC WASTE FROM CORES TAKEN FROM FIELD CELLS 2, 3, AND 5

d-Spacing (Å)	Crystalline Component
9.71	ettringite
7.59	gypsum
5.59	ettringite
4.78	brucite
4.29	gypsum
3.86	calcite, ettringite
3.80	gypsum
3.49	ettringite
3.34	quartz
3.07	gypsum, calcite
2.87	gypsum
2.79	gypsum, ettringite
2.69	gypsum
2.59	gypsum
2.56	ettringite
2.52	calcite
2.49	gypsum, calcite
2.45	gypsum, quartz
2.37	brucite
2.29	calcite, quartz
2.21	gypsum, ettringite
2.10	calcite
2.08	gypsum
2.07	gypsum
1.98	gypsum
1.90	gypsum, calcite
1.88	gypsum, calcite
1.82	quartz
1.81	gypsum
1.80	brucite
1.78	gypsum
1.66	gypsum
1.64	gypsum
1.62	gypsum
1.58	gypsum
1.50-1.49	brucite
1.46	gypsum

($CaMg(CO_3)_2$) and beta-calcium silicate (β-$CaSiO_3$) were also found to be present, as well as possibly $CaSO_4 \cdot MgSO_4$. Unequivocal identification of $CaSO_4 \cdot 3MgSO_4$ was difficult in these samples due to the complexity of the X-ray diffraction pattern.

The major components in runs 80 and 81 of Cyclone No. 3 are quartz, anhydrite, and calcium silicate. $CaSO_4 \cdot 3MgSO_4$, hematite, and magnetite are also present. Dolomite is also identifiable.

C.3.1.3 X-Ray Analysis of Alliance AFBC Waste

The crystalline species identified by x-ray diffraction analysis of the Alliance AFBC waste before and after leaching are listed in Table C-9. The species identified in the unleached waste are anhydrite, portlandite, quartz, hematite, calcite, and lime.

A waste representativeness test was performed to evaluate the effectiveness of techniques employed to obtain representative samples of solid wastes. Five randomly selected samples of unleached Alliance AFBC waste were examined by X-ray diffraction. All five samples were nearly identical in the X-ray diffraction patterns, which indicated that each sample contained approximately the same ratio of individual mineral components. The d-spacings and mineral identification for samples examined in the representativeness test are shown in Table C-10. This diffraction study was performed on a different instrument much later in the program than the sample used as the unleached Alliance AFBC waste sample in Table C-9. Not only was the agreement among these five samples very good, but the agreement with the sample analyzed several months before was also very good indicating the presence of the same crystalline components.

After leaching, the species found were gypsum, portlandite, quartz, and ettringite. Ettringite is the product of chemical reactions of calcium hydoxide, calcium sulfate dihydrate, and aluminum compounds present in the waste. These aluminum compounds tend to occur in the amorphous state and can rarely be identified in X-ray powder diffraction patterns. Ettringite is a

TABLE C-9. INTERPRETATION OF X-RAY POWDER DIFFRACTION PATTERNS OF ALLIANCE AFBC WASTE BEFORE AND AFTER LEACHING

Before Leaching		After Leaching	
d-Spacing (Å)	Crystalline Component	d-Spacing (Å)	Crystalline Component
4.950	portlandite	9.600	ettringite
4.260	quartz	7.480	gypsum
3.863	anhydrite	5.535	ettringite
3.660	hematite	4.897	ettringite, portlandite
3.490	anhydrite	4.668	ettringite
3.349	quartz	4.267	gypsum, quartz
3.129	anhydrite, portlandite	3.847	ettringite, calcite
3.046	calcite	3.783	ettringite; gypsum
2.855	anhydrite	3.588	ettringite
2.778	lime, anhydrite	3.451	ettringite
2.696	hematite	3.324	quartz
2.627	portlandite	3.207	ettringite
2.520	hematite	3.097	portlandite
2.473	anhydrite, quartz	3.046	gypsum
2.409	lime	3.035	ettringite, calcite
2.336	anhydrite	2.867	gypsum
2.209	anhydrite, hematite	2.753	ettringite
2.184	anhydrite	2.688	ettringite, gypsum, hematite
2.088	anhydrite	2.620	portlandite
2.030	-	2.616	ettringite
1.993	anhydrite	2.540	ettringite
1.938	anhydrite	2.513	ettringite, hematite
1.927	portlandite	2.495	calcite
1.912	-	2.279	calcite
1.817	anhydrite	2.194	hematite
1.839	hematite	2.134	-
1.793	portlandite	2.095	calcite
1.744	anhydrite, portlandite	2.088	gypsum
1.702	lime, hematite	2.073	gypsum
1.652	anhydrite	2.025	-
1.487	anhydrite, hematite	1.927	portlandite
1.452	lime, hematite	1.913	calcite
		1.898	gypsum
		1.875	gypsum, calcite
		1.839	hematite
		1.796	portlandite
		1.694	portlandite, hematite
		1.485	portlandite, hematite
		1.452	portlandite, hematite

TABLE C-10. INTERPRETATION OF X-RAY POWDER DIFFRACTION PATTERN OF FIVE UNLEACHED SAMPLES OF ALLIANCE AFBC WASTE USED IN THE REPRESENTATIVENESS TEST

d-Spacing (Å)	Crystalline Component
4.90	portlandite
4.25	quartz
3.88	calcite, anhydrite
3.68	hematite
3.34	quartz
3.11	anhydrite, portlandite
3.035	calcite
2.62	portlandite
2.515	calcite, hematite
2.46	quartz anhydrite
2.40	lime
2.33	anhydrite
2.285	calcite, hematite, quartz
2.21	hematite
2.19	anhydrite
2.09	calcite, hematite
1.99	anhydrite
1.93	calcite, anhydrite, portlandite
1.87	calcite, anhydrite
1.84	hematite, anhydrite
1.79	portlandite
1.74	anhydrite
1.697	lime, portlandite, hematite
1.647	anhydrite
1.596	hematite, anhydrite
1.559	anhydrite, portlandite
1.522	anhydrite
1.485	hematite, anhydrite, portlandite
1.450	hematite, lime, anhydrite
1.386	lime
1.318	anhydrite, portlandite
1.310	hematite
1.276	anhydrite
1.200	lime, anhydrite
1.164	hematite

minor component of hydrated Portland cement. It often forms in mixtures of coal fly ash, and wet scrubber sludge.

Core samples of the leached Alliance AFBC waste were removed from three field cells (Cells 13, 14, and 17). The X-ray diffraction study of these solids (Table C-11) showed very similar d-spacings and mineral ratios. These samples contained primarily portlandite, gypsum, and calcite with smaller amounts of quartz, ettringite and hematite. The waste removed from Cell 13 may have contained slightly more portlandite while the waste from Cell 17 contained slightly less gypsum, but these differences were very slight.

Two additional batch leaching tests were performed with the Alliance AFBC waste followed by analysis of leached solids by X-ray diffraction. These tests involved batch equilibrations of leachate produced from two disposal media (shale and sandstone) with Alliance AFBC wastes. High concentrations of several constituents in the leachates from laboratory control columns containing only disposal media indicated that the disposal media could contribute these constituents to field leachates. The effect of using a disposal medium leachate instead of deionized water to leach Alliance AFBC waste apparently was the inhibition of the hydration reactions of lime and anhydrite. While lime and anhydrite are completely hydrated in the field cell waste and in the waste leached by the original batch leaching protocol with deionized water, both lime and anhydrite remain in the Alliance AFBC waste leached with media leachate. All other identifiable crystalline components were the same in all three leaching regimes. These included gypsum, portlandite, quartz, ettringite, hematite, and calcite. The d-spacings and mineral identifications are listed in Table C-12 for the Alliance AFBC wastes leached with sandstone and shale leachate.

C.3.1.4 X-Ray Analysis of Georgetown AFBC Waste

The d-spacings and mineral identification for the Georgetown AFBC waste before and after leaching are listed in Table C-13. The unleached Georgetown AFBC waste contained portlandite, anhydrite, quartz, calcite, lime, and hematite. These are the same crystalline components present in the

TABLE C-11. INTERPRETATION OF X-RAY POWDER DIFFRACTION PATTERN OF LEACHED ALLIANCE AFBC WASTE FROM CORES TAKEN FROM FIELD CELLS 13, 14, AND 17

d-Spacing (Å)	Crystalline Component
9.65	ettringite
7.60	gypsum
5.59	
4.91	portlandite, ettringite
4.68	ettringite
4.58	
4.28	gypsum
3.85	calcite
3.80	gypsum
3.46	ettringite
3.34	quartz
3.22	ettringite
3.11	portlandite
3.05	calcite
2.87	gypsum
2.79	gypsum
2.75	ettringite
2.69	hematite, gypsum, ettringite
2.63	portlandite, ettringite
2.56	ettringite, gypsum
2.51	hematite, calcite
2.45	portlandite
2.28	calcite
2.20	gypsum, ettringite, hematite
2.09	gypsum, calcite
2.07	gypsum
1.92	portlandite
1.90	gypsum
1.88	gypsum, calcite
1.84	hematite
1.81	gypsum
1.79	portlandite
1.68	hematite, portlandite
1.66	gypsum
1.62	gypsum
1.48	hematite, portlandite
1.45	hematite, portlandite

TABLE C-12. INTERPRETATION OF X-RAY POWDER DIFFRACTION PATTERN OF ALLIANCE AFBC WASTE LEACHED WITH SANDSTONE AND SHALE LEACHATE

Sandstone Leachate		Shale Leachate	
d-spacing (Å)	Crystalline Component	d-spacing (Å)	Crystalline Component
9.65	ettringite	9.71	ettringite
7.56	gypsum	7.62	gypsum
5.59	ettringite	5.60	ettringite
4.90	ettringite, portlandite	4.92	ettringite, portlandite
4.66	ettringite	4.67	ettringite
4.27	gypsum	4.29	gypsum
3.85	ettringite, calcite, gypsum	3.86	ettringite, calcite, gypsum
3.67	hematite, ettringite	3.48	anahydrite, ettringite
3.57	ettringite	3.35	quartz
3.46	anhydrite, ettringite	3.23	ettringite
3.34	quartz	3.06	gypsum, calcite
3.22	ettringite	2.88	gypsum
3.11	portlandite	2.77	ettringite, lime
3.04	gypsum, calcite	2.70	hematite, gypsum, ettringite
2.87	gypsum	2.63	ettringite, portlandite
2.84	anhydrite	2.56	ettringite
2.76	ettringite, lime	2.53	hematite, calcite
2.70	hematite, gypsum, ettringite	2.41	lime, ettringite
2.62	ettringite, portlandite	2.29	calcite
2.55	ettringite	2.20	hematite, anhydrite, ettringite
2.51	hematite, calcite	2.15	ettringite
2.40	lime, ettringite	2.09	gypsum
2.34	anhydrite	1.93	portlandite
2.29	calcite	1.92	calcite
2.20	hematite, anhydrite, ettringite	1.88	calcite, anhydrite, gypsum
2.14	ettringite	1.84	hematite
2.09	gypsum	1.81	quartz
1.93	portlandite	1.80	portlandite
1.92	calcite	1.66	anhydrite
1.88	calcite, anhydrite, gypsum	1.61	hematite
1.84	hematite	1.48	hematite, portlandite
1.80	portlandite	1.45	lime, hematite,
1.69	lime, hematite, portlandite	1.30	calcite
1.66	anhydrite		
1.60	hematite		
1.48	hematite, portlandite		
1.45	lime, hematite, portlandite		
1.31	calcite		

TABLE C-13. INTERPRETATION OF X-RAY POWDER DIFFRACTION PATTERN OF GEORGETOWN AFBC WASTE BEFORE AND AFTER LEACHING

Before Leaching		After Leaching	
d-spacing (Å)	Crystalline Component	d-spacing (Å)	Crystalline Component
4.90	portlandite	9.70	ettringite
3.495	anhydrite	7.62	gypsum
3.34	quartz	5.641	ettringite
3.035	calcite	4.92	portlandite, ettringite
2.85	anhydrite	4.66	ettringite
2.77	lime	4.22	gypsum
2.70	hematite	3.86	anhydrite, ettringite
2.62	portlandite	3.78	gypsum
2.515	calcite	3.67	hematite, ettringite
2.46	anhydrite, quartz	3.59	ettringite
2.40	lime	3.46	anhydrite
2.33	anhydrite	3.34	quartz
2.285	calcite, hematite, quartz	3.24	ettringite
2.21	hematite, anhydrite	3.11	portlandite
2.19	anhydrite	3.03	calcite, gypsum
2.09	calcite, hematite, portlandite	2.85	anhydrite, gypsum
1.93	calcite, anhydrite, portlandite	2.75	ettringite
1.87	calcite, anhydrite	2.71	ettringite, hematite
1.78	portlandite	2.63	portlandite, gypsum
1.74	anhydrite	2.55	ettringite
1.697	lime, portlandite, hematite	2.50	hematite
1.64	anhydrite	2.40	ettringite
1.485	hematite, anhydrite, portlandite	2.34	anhydrite
1.450	hematite, lime, portlandite	2.28	hematite, calcite, quartz
1.386	lime	2.21	anhydrite, ettringite, hematite
1.378	anhydrite, portlandite		
1.276	anhydrate	2.14	ettringite
1.200	lime, anhydrite	2.13	hematite
1.104	hematite, lime, anhydrate	2.10	gypsum, anhydrite
		1.93	portlandite
		1.92	gypsum
		1.875	anhydrite, gypsum
		1.84	hematite
		1.82	gypsum
		1.79	gypsum, portlandite
		1.697	lime, hematite, portlandite
		1.66	anhydrate
		1.60	hematite
		1.485	portlandite, hematite
		1.45	lime, hematite, portlandite
		1.37	lime
		1.31	portlandite
		1.140	hematite, portlandite

Alliance AFBC, but with differences in quantity. The Georgetown AFBC waste contained more portlandite, quartz, and much more lime; it also contained less anhydrite, calcite and hematite than the Alliance AFBC waste.

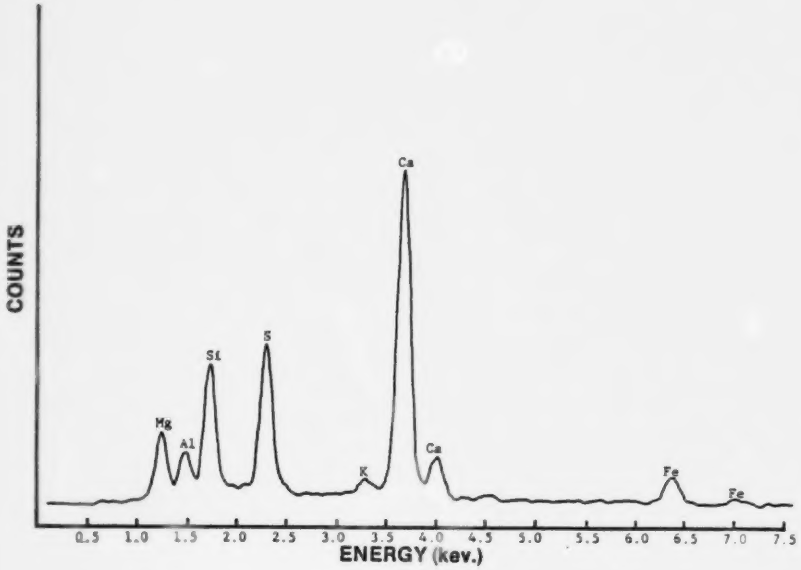
After Step 2 leaching for nine repetitions according to the laboratory protocol, the Georgetown AFBC waste residues contained the crystalline components ettringite, gypsum, portlandite, anhydrite, calcite, quartz and hematite. The only apparent difference between the leached waste residues from Alliance and Georgetown AFBC wastes was the presence of anhydrite in the Georgetwon leached waste.

C.3.2 X-Ray Fluorescence

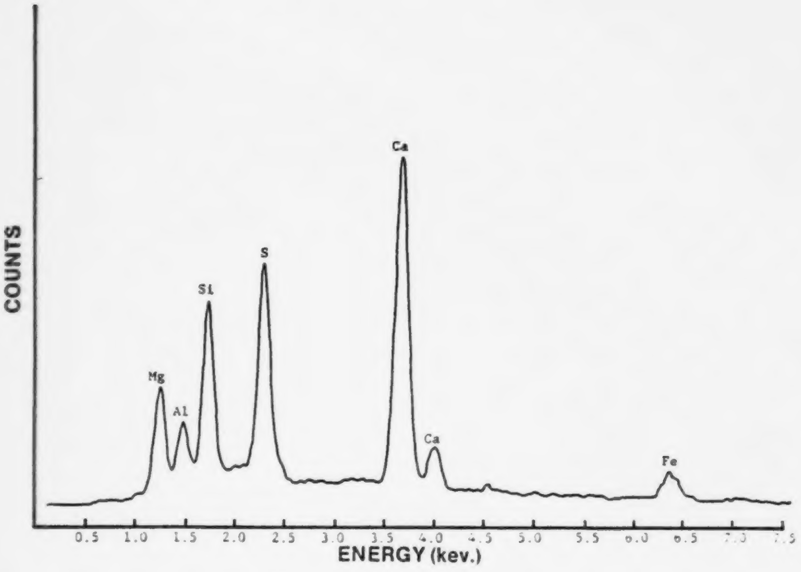
X-ray fluorescence (XRF) spectra were taken of the Exxon PFBC waste, the Alliance AFBC waste, and the Georgetown AFBC waste before and after leaching to determine the elemental chemical profile for fluorine and heavier elements. XRF spectra were also used to determine the representativeness of Alliance AFBC waste samples and the composition of Alliance AFBC waste after leaching with sandstone and shale leachate.

Figure C-1 illustrates the spectra of Exxon PFBC waste before and after leaching. There are no major differences in the elemental compositions discernible by XRF analysis of this waste before and after leaching. The small amount of potassium present in the unleached waste did disappear during repetitive leaching. The relative intensities of peaks did not undergo any significant changes with leaching. The depletion of these species in the leached solid was expected because of its solubility. None of these elements was selectively leached in greater quantities from the bulk of the waste.

Figure C-2 shows the spectra of Alliance AFBC waste before and after leaching. Although the spectra of the waste before and after leaching are generally similar, there are some minor differences in the relative elemental concentrations. Reduced intensities for aluminum, iron and potassium indicate the depletion of these species with leaching. The similar spectra for other

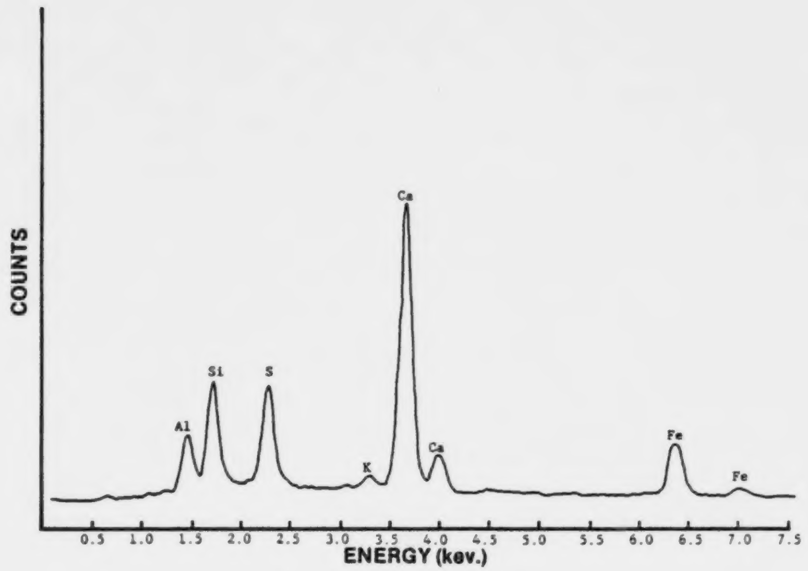


a. **Before Leaching**

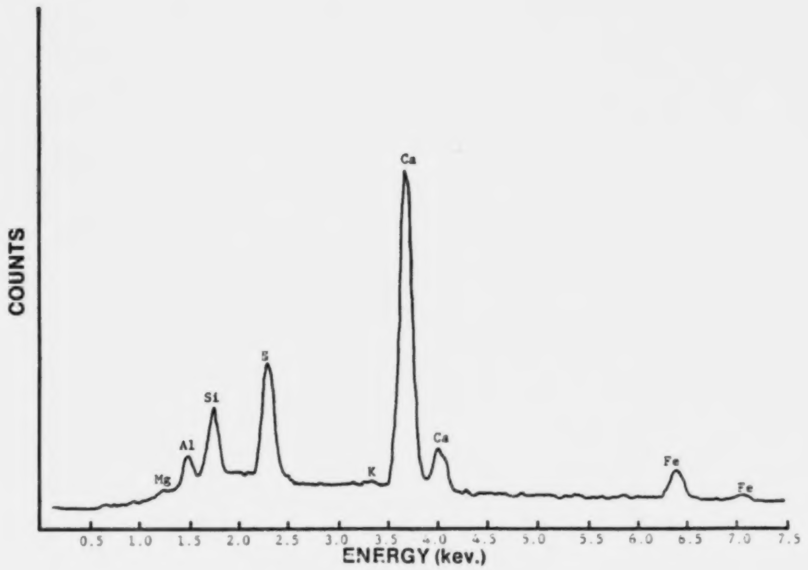


b. **After Leaching**

Figure C-1. **X-Ray Fluorescence Spectra for Exxon PFBC Waste Before and After Leaching.**



a. Before Leaching



b. After Leaching

Figure C-2. X-Ray Fluorescence Spectra for Alliance AFBC Waste Before and After Leaching.

elements before and after leaching is evidence that significant depletion has not occurred.

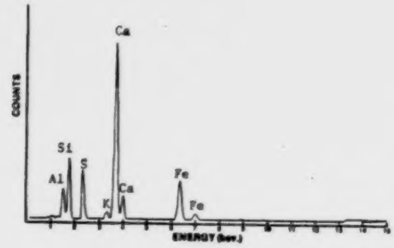
Figure C-3 shows the XRF spectra of five randomly selected samples of Alliance AFBC waste. This analysis was performed to determine the effectiveness of the techniques used to obtain representative samples of solid wastes for the laboratory batch leaching protocol. These results show that the sampling preparation techniques produced representative samples. The XRF scans were extremely similar with similar ratios of aluminum, silicon, sulfur, potassium, calcium, and iron in each of the five samples.

The Alliance AFBC waste was used in two additional leaching tests after which the waste residue was analyzed by XRF. In these two tests the waste was leached repeatedly with the leachate from sandstone and shale. These two leached wastes had XRF spectra that are almost identical (Figure C-4). The shale and sandstone leachate used to leach the waste did not differ in their effect upon the elemental composition of the waste after leaching. These leached waste residues were very similar to the residue from the Alliance AFBC waste leached with water (see Figure C-3). Aluminum and silicon appeared to diminish in relative concentration as the waste was leached with all three leachates.

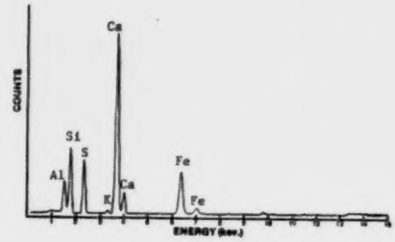
Figure C-5 shows the spectra of Georgetown AFBC waste before and after leaching. The Georgetown AFBC waste was leached in both the ground and unground state. There were no major differences between the XRF spectra for the leached ground waste and the leached unground waste. This observation is consistent with the fact that no appreciable difference is seen in leachate compositions whether ground or unground waste was leached in the laboratory protocol.

C.3.3 Electron Microprobe Analysis

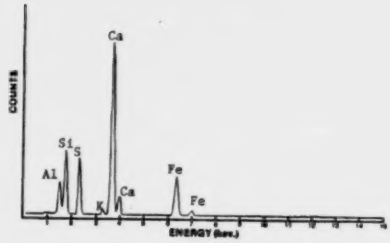
The concentrations of several elements at different depths within the particles of the unleached Exxon PFBC waste were determined by electron microprobe analysis. The elemental composition of two near-surface layers was



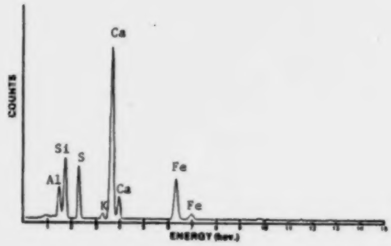
Alliance AFBC Waste: Sample Lot "A"



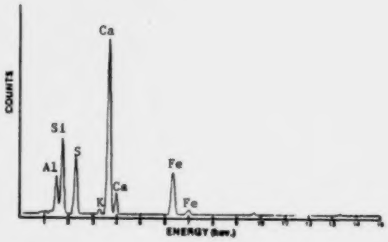
Alliance AFBC Waste: Sample Lot "B"



Alliance AFBC Waste: Sample Lot "C"



Alliance AFBC Waste: Sample Lot "D"



Alliance AFBC Waste: Sample Lot "E"

Figure C-3. X-Ray Fluorescence Spectra to Determine Representativeness of Alliance AFBC Waste Samples.

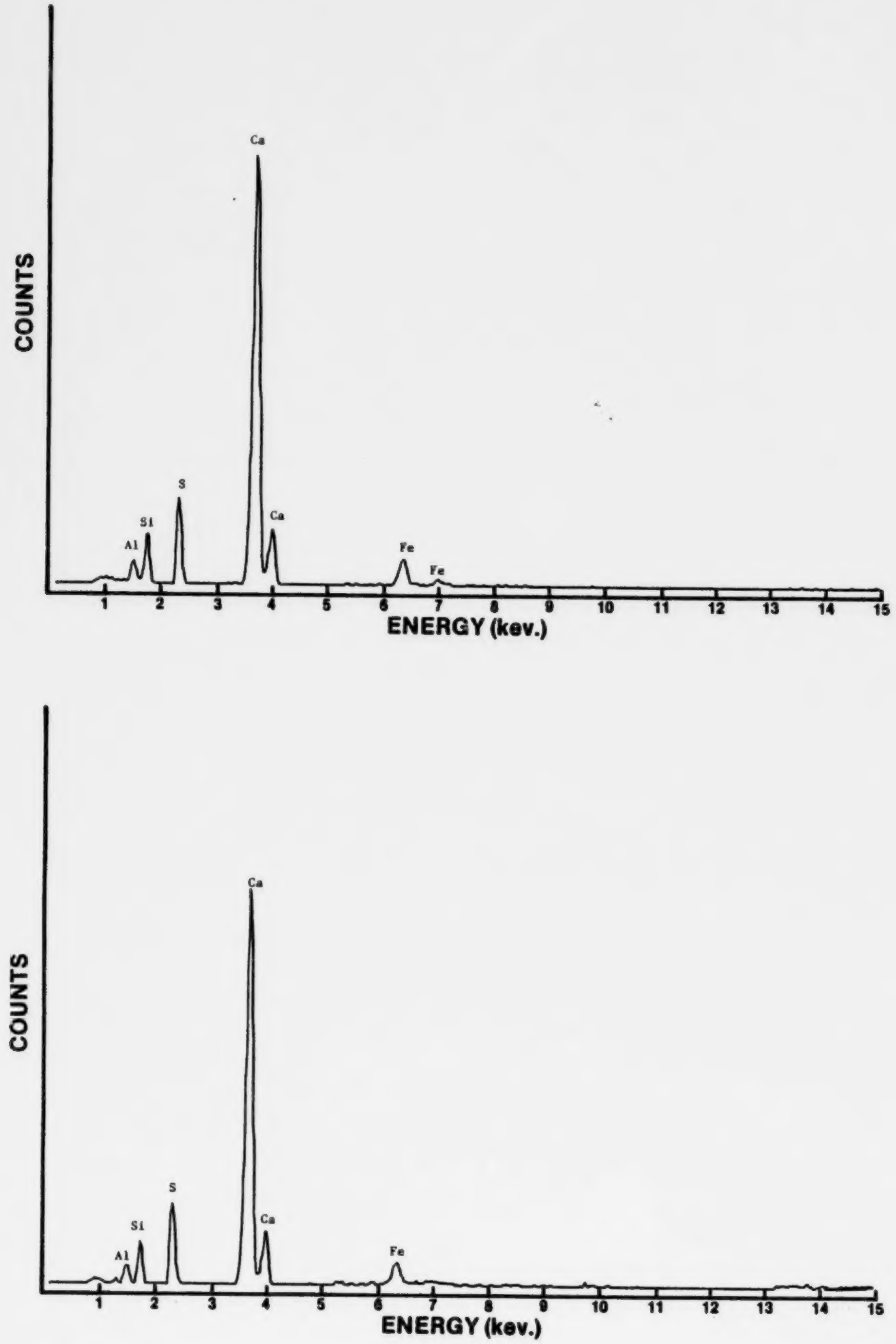
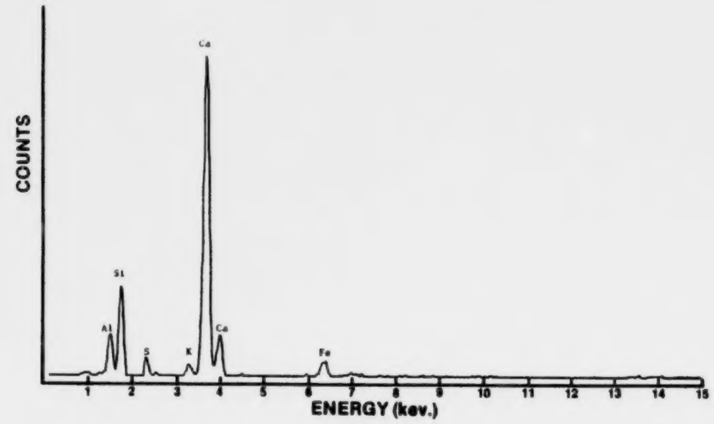
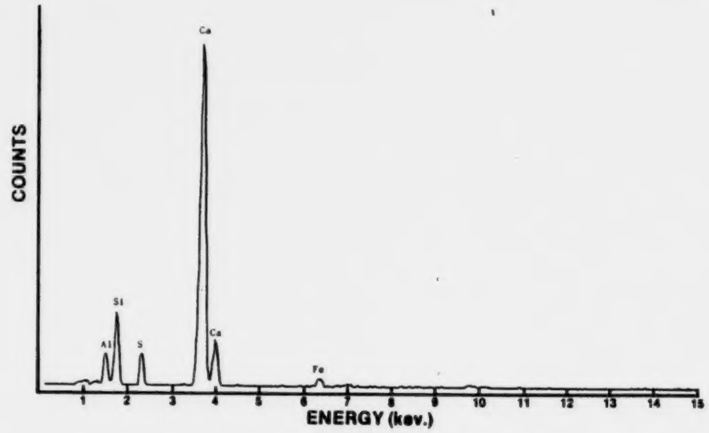


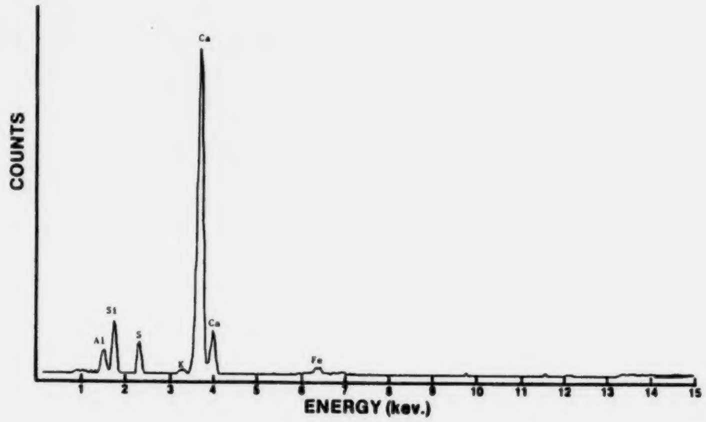
Figure C-4. X-Ray Fluorescence Spectra for Alliance AFBC Waste Leached with Sandstone Leachate (top) and Shale (bottom).



Unleached Georgetown AFBC Waste



Ground, Leached Georgetown AFBC Waste



Unground, Leached Georgetown AFBC Waste

Figure C-5. X-Ray Fluorescence Spectra for Leached and Unleached Georgetown AFBC Waste.

determined for magnesium, aluminum, silicon, sulfur, potassium, calcium, and iron. Only the unleached PFBC wastes was analyzed by this method because it was found that the information yielded did not warrant analysis of leached PFBC waste or of the Alliance and Georgetown AFBC wastes. The preliminary studies undertaken indicated qualitatively that all elements of analysis except iron appeared to have similar concentrations in the two layers examined. More iron apparently was present in the interior layer than in the exterior layer.

C.3.4 Solid Sample Chemical Composition

Chemical analyses were performed on the following solid samples:

- Feedstocks to the Exxon PFBC plant;
- Separate waste stream samples from the PFBC plant;
- Unleached PFBC mixed (composite) waste;
- Leached PFBC mixed waste (from Steps 2 and 5 of the laboratory protocol);
- Leached PFBC mixed waste (from Field Cells 2, 3, and 5);
- Five randomly selected unleached Alliance AFBC waste;
- Leached Alliance AFBC waste (Step 2 of the laboratory protocol);
- Leached Alliance AFBC waste (Step 2 of the laboratory protocol) that was ground and unground.
- Leached AFBC mixed waste (from field cells 13, 14, and 17); and

- AFBC mixed waste leached in a modified Step 2 and 5 of the laboratory protocol using sandstone and shale leachate.

- Unleached and leached Georgetown AFBC waste.

The results of the chemical analyses are presented in percent (g/100g) for the major constituents and in milligrams per kilogram (mg/kg) for the minor constituents. In some cases, concentration of a parameter is reported as less than a certain solid detection limit. The solid detection limit is a function of the analytical detection limit for the parameter analyzed in the digest and the dilution factor arising from the digestion of the solid samples.

C.3.4.1 Exxon PFBC Waste

The feedstocks to the Exxon PFBC plant which were analyzed were Illinois No. 6 coal from the Monterey mine (8 X 50 mesh) and Pfizer 1337 dolomite from Ohio (8 X 25 mesh). The solid sample analysis of the PFBC feed coal and feed dolomite (Table C-14) yield a preliminary estimate of the source of contaminants in the waste. It should be noted that this solid sample analysis indicates the total amount of a species present in the solid, which is not to be confused with the amount leachable. The feed coal is the primary source of Al, Fe, Na, Si, Be, Cok, Mo, and Ni. If a waste leachate has excessively high concentrations of these elements, it may be possible to change the coal feed or feed rate to reduce these contaminants. The dolomite would be expected to be the primary contributor of Ca, Mg, Ba, Cr, Cu, Sr, V, and Zn.

The PFBC waste used for the solids chemical analysis was composed of waste material from runs 79, 80, and 81. As noted in Appendix A, the composite sample was prepared from the following components:

- Bed draw, Run 79;

- Bed draw, Run 80;

TABLE C-14. SOLIDS ANALYSIS OF EXXON PFBC FEED COAL AND FEED DOLOMITE

Sample Description:	Feed Coal	Feed Dolomite
Al (g/100 g)[1]	0.94	0.114
Ca "	0.18	22
Fe "	1.07	0.058
K "	0.18	1.8
Mg "	0.074	13.1
Na "	0.073	0.037
Si "	2.0	0.33
SO_4 "	–	–
Ti "	0.052	0.0073
B (mg/kg)[2]	–	–
Ba "	45	103
Be "	2.6	<1.2
Cd "	–	–
Cl "	–	–
Co "	3.9	<15
Cr "	26	40
Cu "	11	21
F "	–	–
Li "	<1	<2.5
Mn "	29	54
Mo "	11	<2.4
Ni "	19	<2.4
Sr "	28	67
V "	26	54
Zn "	19	85

[1] g species per 100 g solid sample.

[2] mg species per kg solid sample.

- Cyclone No. 2, Run 79;
- Cyclone No. 2, Run 80;
- Cyclone No. 3, Run 80; and
- Cyclone No. 3, Run 81.

Bed draw, Cyclone No. 2, and Cyclone No. 3 composites, respectively, were prepared. The PFBC mixed waste was formed by mixing two parts bed draw composite, one part Cyclone No. 2 composite, and 0.1 part Cyclone No. 3 composite.

The solid sample analysis of the PFBC bed draw from runs 79, 80 and a composite are given in Table C-15. The elemental components were generally the same for run 79 and run 80. Variations in the concentrations of Ba, Be, Cu, Mn, Mo, V, and Zn were observed.

The solid sample analysis of PFBC Cyclone No. 2 from runs 79 and 80 are shown in Table C-16. Of the major elements, only the sodium concentration differed in the two runs. Strontium also varied in concentration in the two runs. All other elemental concentrations were generally the same. The solid sample analysis of PFBC Cyclone No. 3 from runs 80 and 81 are shown in Table C-17. Of the major elements, differences were observed in the magnesium and silicon content between the two runs. These two runs also resulted in different Ba, Cr, Cu, Li, Ni, B, F, and Zn concentrations.

The solid sample analysis of unleached and leached PFBC mixed wastes are given in Table C-18. The leached PFBC waste was from seven repetitions of protocol Step 2 (seven-day) leaching.Of the major elements, Al, Fe, K, Na, Si, and Ti did not appear to be significantly depleted. Calcium, magnesium, and sulfate concentrations in the solids were lower after leachate interaction. Concentrations of Cr, Cu, Li, Mn, Mo, and Ni in the solids did not change significantly with leaching, whereas concentrations of strontium, vanadium, and boron in the solids were notably reduced. Some depletion of beryllium, fluoride, and zinc also occurred.

TABLE C-15. SOLIDS ANALYSIS OF EXXON PFBC BED DRAW

Sample I.D.:	–	–	–	
Waste Type:	PFBC Component	PFBC Component	PFBC Components	
Description:	Bed Draw Run No. 79	Bed Draw Run No. 80	Bed Draw Composite: Runs 79 and 80	
Protocol Step:	Unleached	Unleached	Unleached	
			Replicate Analyses	
Al (g/100 g)[1]	1.38	1.80	–	–
Ca "	24.0	23.0	–	–
Fe "	2.0	2.9	–	–
K "	2.1	2.0	–	–
Mg "	13.6	13.6	–	–
Na "	0.138	0.120	–	–
Si "	3.1	3.8	–	–
SO_4 "	–	–	23	24
Ti "	0.108	0.138	–	–
B (mg/kg)[2]	–	–	970	1200
Ba "	108	46	–	–
Be "	5.4	8.0	–	–
Cd "	–	–	–	–
Cl "	–	–	300	300
Co "	<15	<15	–	–
Cr "	98	110	–	–
Cu "	88	57	–	–
F "	–	–	128	118
Li "	<2.5	<2.5	–	–
Mn "	103	134	–	–
Mo "	18	27	–	–
Ni "	37	42	–	–
Sr "	136	146	–	–
V "	116	137	–	–
Zn "	210	280	–	–

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[1] g species per 100 g solid sample.

[2] mg species per kg solid sample.

TABLE C-16. SOLIDS ANALYSIS OF WASTE FROM EXXON PFBC CYCLONE NO. 2

Sample I.D.:	–	–	–	
Waste Type:	PFBC Component	PFBC Component	PFBC Components	
Description:	2nd Cyclone Run No. 79	2nd Cyclone Run No. 80	2nd Cyclone Composite: Runs 79 and 80	
Protocol Step:	Unleached	Unleached	Unleached	
			Replicate Analyses	
Al (g/100 g)[1]	5.3	6.5	–	–
Ca "	13.8	11.2	–	–
Fe "	5.3	6.0	–	–
K "	2.3	2.4	–	–
Mg "	8.2	6.8	–	–
Na "	1.07	0.52	–	–
Si "	11.9	14.1	–	–
SO_4 "	–	–	20	19
Ti "	0.26	0.30	–	–
B (mg/kg)[2]	–	–	250	250
Ba "	175	210	–	–
Be "	16	17	–	–
Cd "	–	–	–	–
Cl "	–	–	330	310
Co "	17	17	–	–
Cr "	135	144	–	–
Cu "	70	79	–	–
F "	–	–	10.0	19.7
Li "	40	50	–	–
Mn "	143	190	–	–
Mo "	45	35	–	–
Ni "	86	94	–	–
Sr "	220	110	–	–
V "	170	190	–	–
Zn "	220	230	–	–

[1] g species per 100 g solid sample.

[2] mg species per kg solid sample.

TABLE C-17. SOLIDS ANALYSIS OF WASTE FROM EXXON PFBC CYCLONE NO. 3

Sample I.D.:	–	–	–	
Waste Type:	PFBC Component	PFBC Component	PFBC Components	
Description:	3rd Cyclone Run No. 80	3rd Cyclone Run No. 81	3rd Cyclone Composite: Runs 80 and 81	
Protocol Step:	Unleached	Unleached	Unleached	
			Replicate Analyses	
Al (g/100 g)[1]	8.0	5.9	–	–
Ca "	6.0	10.5	–	–
Fe "	5.9	4.9	–	–
K "	2.5	2.2	–	–
Mg "	2.7	6.6	–	–
Na "	0.87	0.58	–	–
Si "	17.2	12.2	–	–
SO_4 "	–	–	23	21
Ti "	0.59	0.41	–	–
B (mg/kg)[2]	–	–	270	1050
Ba "	320	170	–	–
Be "	23	20	–	–
Cd "	–	–	–	–
Cl "	–	–	160	150
Co "	35	33	–	–
Cr "	510	350	–	–
Cu "	144	95	–	–
F "	–	–	31	87
Li "	50	<2.5	–	–
Mn "	260	210	–	–
Mo "	35	42	–	–
Ni "	300	200	–	–
Sr "	310	250	–	–
V "	260	225	–	–
Zn "	25	270	–	–

[1] g species per 100 g solid sample.

[2] mg species per kg solid sample.

TABLE C-18. SOLIDS ANALYSIS OF UNLEACHED AND LEACHED EXXON PFBC MIXED WASTE

Sample I.D.:	S000100		S277100	
Waste Type:	PFBC		PFBC	
Description:	Composite Waste		Composite Waste	
Protocol Step:	Unleached		2	
Leaching Time:	–		7d	
No. Repetitions:	–		7[1]	
	Replicate Analyses		Replicate Analyses	
Al (g/100 g)[2]	2.4	2.4	2.7	2.7
Ca "	22	22	11.7	11.3
Fe "	3.0	3.0	4.0	4.0
K "	2.1	2.2	2.2	2.1
Mg "	11.9	11.6	8.0	7.8
Na "	0.23	0.81	0.085	0.035
Si "	5.1	5.2	6.7	6.5
SO_4 "	22.0	23.0	20.0	20.0
Ti "	0.158	0.160	0.225	0.227
Ag (mg/kg)[3]	<0.250	<0.250	–	–
B "	650	800	380	490
Ba "	114	59	158	137
Be "	8.8	8.5	6.6	6.6
Cd "	0.44	0.43	–	–
Cl "	280	285	<40	<40
Co "	13	<14.1	12	10
Cr "	118	139	91	93
Cu "	55	62	49	70
F "	180	180	110	120
Li "	<2.5	<2.5	<2.5	<2.5
Mn "	129	127	129	135
Mo "	24	28	35	34
Ni "	53	59	79	81
Sr "	156	159	89	90
V "	140	132	57	63
Zn "	219	353	256	239

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[1] Cumulative volume-per-mass ratio: 80 mL H^2O per gram of waste.

[2] g species per 100 g solid sample.

[3] mg species per kg solid sample.

The solid sample analyses of leached PFBC waste removed from field cells 2, 3, and 5 are given in Table C-19. Concentrations of Ca, K, Mg, Na, and Si were significantly depleted after leaching in the PFBC field cells. Cl, Cu, Co, Sr, and Zn concentrations in the solids were also somewhat depleted during leaching. The different overlying disposal medium layers in the field cells did not significantly affect the waste solids content.

C.3.4.2 Alliance AFBC Waste

Only the composite sample of the Alliance AFBC waste was analyzed for solid sample composition; the component streams were not analyzed individually. The leached wastes analyzed were from Step 2 (repetition seven) of the laboratory protocol, from the field cells containing Alliance AFBC wastes, and from the modified laboratory protocol using sandstone and shale leachate instead of deionized water.

A comparison of the solid composition of unleached and leached (protocol Step 2) Alliance AFBC waste (Table C-20) shows that there is a major loss of sulfate and strontium in the solids after leaching. Calcium, chloride, molybdenum, and zinc, which are all very soluble species, were also significantly depleted after leaching.

The results given in Table C-20 are for an unleached representative sample of the Alliance AFBC waste and a different leached representative AFBC sample. It is conceivable that the starting wastes - leached and unleached - differed in composition due to sample inhomogeneity. The replicate analysis of the leached and unleached Alliance AFBC waste showed good precision except for the boron and vanadium in the unleached waste and copper in the leached waste. In comparing the composition data of the unleached waste in Table C-20 with the average chemical compositon for the unleached waste in Table C-21, there were some differences. Major differences occurred in concentrations of Na, Ag, B, Be, Cr, and V. These analyses, performed over a year apart, were subject to sample inhomogeneity and possibly to instrumental variation.

TABLE C-19. SOLIDS COMPOSITION OF LEACHED EXXON PFBC WASTE CORES FROM FIELD CELLS 2, 3, AND 5

	Field Cell 2[1]	Field Cell 3[1]	Field Cell 5[1]
Al (g/100 g)[2]	2.1	2.7	2.1
Ca "	14	15	15
Fe "	3.1	3.6	3.0
K "	2.9	3.1	2.8
Mg "	7.7	7.8	7.6
Na "	0.21	0.27	0.22
Si "	3.4	2.3	5.3
SO "	19	19	16
Ti "	0.12	0.15	0.12
Ag (mg/kg)[3]	<0.5	<0.5	<0.5
B "	700	600	540
Ba "	180	175	150
Be "	6.2	8.0	6.5
Cd "	<0.5	0.5	<0.5
Cl "	97	140	170
Co "	1.7	7.8	9.1
Cr "	100	140	100
Cu "	17	31	34
F "	280	240	210
Li "	17	26	25
Mn "	120	110	100
Mo "	18	24	24
Ni "	48	54	46
Sr "	56	68	56
V "	63	90	87
Zn "	160	160	140

[1] Cumulative volume-per-mass ratio: 0.02 mL rainfall per gram of waste.

[2] g species per 100 g solid sample.

[3] mg species per kg solid sample.

TABLE C-20. SOLIDS COMPOSITION OF UNLEACHED AND LEACHED ALLIANCE AFBC WASTE

Sample I.D.:	S0003000		S279300	
Waste Type:	Alliance AFBC		Alliance AFBC	
Description:	Composite Waste		Composite Waste	
Protocol Step:	Unleached		2	
Leaching Time:	-		7d	
No. Repetitions:	-		9[1]	
	Replicate Analyses		Replicate Analyses	
Al (g/100 g)[2]	1.95	1.95	1.80	2.56
Ca "	31	31	21	20
Fe "	5.3	5.3	5.3	5.3
K "	0.42	0.43	0.32	0.40
Mg "	0.47	0.47	0.43	0.52
Na "	<0.001	<0.001	<0.001	0.06
Si "	4.1	4.2	4.2	5.2
SO_4 "	12.9	12.4	1.36	1.39
Ti "	0.15	0.15	0.138	0.20
B (mg/kg)[3]	410	190	170	260
Ba "	289	288	232	249
Be "	5.0	4.6	5.1	5.3
Cd "	0.15	0.19	-	-
Cl "	820	860	420	420
Co "	9	9	10.9	12.5
Cr "	29	34	59	40
Cu "	47	30	9.7	98.2
F "	160	140	190	180
Li "	<2.5	<2.5	<2.5	<2.5
Mn "	610	588	649	656
Mo "	26	28	17	18
Ni "	38	43	38	43
Sr "	821	817	256	258
V "	24	9.6	38	39
Zn "	64	73	54	56

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[1] Cumulative volume-per-mass ratio: 100 mL H_2O per gram of waste

[2] g species per 100 g solid sample.

[3] mg species per kg solid sample.

TABLE C-21. SOLIDS COMPOSITION OF ALLIANCE AFBC WASTE SAMPLES RANDOMLY SELECTED FOR REPRESENTATIVENESS TEST

Sample I.D.: 50003
Description: Unleached Alliance AFBC Waste

		Sample A	Sample B	Sample C	Sample D	Sample E	Mean	Standard Deviation (%)[1]
Al	(g/100 g)[2]	1.9	1.9	1.8	1.8	1.8	1.8	2
Ca	"	34	35	34	33	34	34	2
Fe	"	5.2	5.2	5.1	5.1	5.1	5.1	1
K	"	0.34	0.38	0.32	0.31	0.30	0.33	8
Mg	"	0.38	0.40	0.37	0.36	0.36	0.37	4
Na	"	0.14	0.13	0.11	0.10	0.092	0.11	14
Si	"	3.6	3.9	3.6	3.6	3.6	3.7	3
SO_4	"	12.7	12.3	10.1	14.2	12.6	12.7	7
Ti	"	0.12	0.12	0.11	0.11	0.11	0.11	4
Ag	(mg/kg)[3]	6.1	7.4	8.0	6.3	7.1	7.0	10
B	"	800	490	370	500	460	520	25
Ba	"	200	210	210	200	170	200	7
Be	"	26	26	36	27	26	26	1
Cd	"	<2	<2	<2	<2	<2	<2	<2
Ca	"	840	860	810	820	850	840	2
Co	"	14	10	11	13	13	12	11
Cu	"	72	74	74	44	41	61	23
Cu	"	31	44	31	15	12	27	40
F	"	280	250	250	270	290	270	5
Li	"	21	15	16	19	21	18	12
Mn	"	560	560	550	570	550	550	2
Mo	"	23	20	20	22	24	22	7
Ni	"	36	32	33	35	38	35	6
Sr	"	560	570	560	540	550	560	2
V	"	62	46	54	60	67	58	11
Zn	"	64	60	72	65	65	65	5

[1] Ave. S.D. = 9%.

[2] g species per 100 g solid sample.

[3] mg species per kg solid sample.

Compared to the solids analysis of the Exxon PFBC waste before and after laboratory leaching, the Alliance waste showed similar leaching trends for Al, Ca, Fe, Na, and Ti in the major constituents. The PFBC waste, of course, showed more magnesium depletion due to the dolomite sorbent used in combustion. The major difference in the chemical components for the two solids appeared to be the amount of sulfate leached. While the PFBC waste contains twice as much sulfate as the Alliance AFBC waste, the sulfate in Alliance waste is depleted much more readily. Comparison of the trace metal behavior of the two wastes shows that the Alliance AFBC waste loses more barium and molybdenum during leaching and much less vanadium and beryllium than the PFBC waste. Other elemental components of waste solids before and after leaching were is very similar for the two wastes.

Differences in the leaching behavior observed in the elemental concentrations in the leachates produced in the laboratory protocol prompted further testing of the representativeness of the solid waste sample preparation. The resultant X-ray diffraction analysis, X-ray fluorescence analyses, and scanning electron micrographs indicated that the solid waste samples were homogeneous from one sample to the next for the five randomly selected waste lots analyzed. The results of the elemental analysis of the five Alliance AFBC waste solids are given in Table C-21. Major variations in the composition were observed for copper and chromium; however, these concentrations are fairly low and a small change in the numbers represents a larger percent deviation.

The elemental compositions of the leached Alliance AFBC waste removed from field cells 13, 14, and 17 are shown in Table C-22. These leached wastes are fairly uniform in composition. Al, Fe, K, Mg, Na, Si, and Ti were depleted more significantly than in the laboratory leaching of the same waste. Of the trace elements, the field cells show a greater depeletion of Ba, Cd, Co, Cu, Mn, Mo, Ni, and Zn in the solid residue.

TABLE C-22. SOLIDS COMPOSITION OF LEACHED ALLIANCE AFBC WASTE CORES FROM FIELD CELLS 13, 14, AND 17[1]

	Field Cell 13	Field Cell 14	Field Cell 17
Al (g/100 g)[2]	1.0	1.4	1.3
Ca "	23	24	21
Fe "	3.0	3.5	3.5
K "	0.24	0.33	0.35
Mg "	0.21	0.23	0.21
Na "	0.11	0.14	0.13
Si "	1.2	1.8	1.5
SO_4 "	11	11	11
Ti "	0.05	0.08	0.07
Ag (mg/kg)[3]	<0.2	<0.2	<0.5
B "	240	280	260
Ba "	190	220	200
Be "	3.8	5.0	5.0
Cd "	0.5	<0.5	<0.5
Cl "	360	270	290
Co "	<1.5	<1.5	2.7
Cr "	16	29	27
Cu "	6.5	7.2	12
F "	160	220	180
Li "	8.7	14	17
Mn "	330	260	250
Mo "	4.9	6.2	7.1
Ni "	13	16	18
Sr "	260	320	240
V "	24	26	33
Zn "	29	39	38

[1] Cumulative, volume-per-mass ratio: 0.01 mL rainfall per gram of waste.

[2] g species per 100 g solid sample.

[3] mg species per kg solid sample.

Compared to the field cells containing Exxon PFBC waste, the Alliance AFBC waste experienced greater depletion of all major species and trace elements; however, the absolute amount available was lower for some elements (e.g., Al, K, Mg, and SO_4) in the Alliance waste than in the Exxon waste.

A special laboratory test was performed in which water was equilibrated with a disposal medium prior to interaction with the Alliance AFBC. The results from leaching the Alliance AFBC waste with shale and sandstone leachate are shown in Table C-23. The elemental concentrations in the Alliance AFBC waste leached with shale and sandstone were very similar. Compared to the protocol Step 2 using deionized water, the use of shale and sandstone leachate did not appear to have a major effect on the solids from the repetition of protocol Step 2. There were some differences observed. More SO_4, B, Be, Cr, and less Al, Ba, and Sr were depleted in the solids after leaching with deionized water than with the shale leachate.

C.3.4.3 Georgetown AFBC Waste

The operating conditions of the Georgetown University AFBC boiler when the waste samples were collected are summarized in Appendix A. The elemental composition of the Georgetown AFBC waste before leaching and after leaching (after nine repetitions of seven-day leachings by protocol Step 2) is given in Table C-24. Of the major species, only aluminum did not appear to be significantly depleted. Ca, Fe, Si, and SO_4 were depleted from the solids during Step 2. Of the trace metals, major quantities of Ag, Ba, Cl, Co, Li, Mo, and Sr were depleted.

Compared to the Exxon PFBC waste, the Georgetown AFBC waste before leaching contained less potassium and magnesium and much less sulfate. The Georgetown AFBC waste also contained less B, Cr, Mo, Ni, V and much less Zn than the PFBC waste. The Georgetown waste, on the other hand, contained more Ag, Cl, F, Mn, Sr, and much more Ba and Li than the PFBC waste.

Compared to the Alliance AFBC waste, the unleached Georgetown waste contained less Na, SO_4, Ba, Cl, Mn, Mo, Ni, Sr, and Zn and more Ag, Be, Cr, F,

TABLE C-23. SOLIDS COMPOSITION OF ALLIANCE AFBC WASTE LEACHED WITH SHALE AND SANDSTONE LEACHATE[1]

Sample ID:	5277308		5277310	
Description:	Alliance AFBC		Alliance AFBC	
Leachate:	Shale Step 1		Sandstone Step 1	
Protocol Step:	2		2	
Leaching Time:	7d		7d	
No. Repetitions:	7		7	
	Replicate Analyses		Replicate Analyses	
Al (g/100 g)[2]	1.7	1.7	1.6	1.6
Ca "	24	24	24	24
Fe "	4.9	4.8	4.5	4.6
K "	0.29	0.27	0.25	0.21
Mg "	0.41	0.42	0.44	0.45
Na "	0 069	0 10	0.06	0.059
Si "	3.4	3.3	3.2	3.2
SO_4 "	6.4	4.7	6.7	7.5
Ti "	0.11	0.11	0.10	0.099
Ag (mg/kg)[3]	4.6	2.6	5.1	1.1
B "	620	660	800	500
Ba "	180	200	200	180
Be "	24	23	22	24
Cd "				
Cl "	410	400	400	420
Co "	8.6	8.2	8.8	11
Cr "	89	92	78	70
Cu "	56	66	39	46
F "				
Li "	4.9	1.6	3.4	7.6
Mn "	530	520	530	530
Mo "	9.6	8.8	9.9	12
Ni "	31	29	29	31
Sr "	170	160	160	160
V "	44	37	43	52
Zn "	56	55	56	59

[1] Cumulative volume-per-mass ratio: 80 mL leachate per gram of waste.

[2] g species per 100 g solid sample.

[3] mg species per kg solid sample.

TABLE C-24. SOLIDS COMPOSITION OF LEACHED AND UNLEACHED GEORGETOWN AFBC WASTE

Sample ID:	500400	5279400		
Waste Type:	Georgetown AFBC	Georgetown AFBC		
Description:	Composite Waste	Composite Waste		
Protocol Step:	Unleached	2		
Leaching Time:		7		
No. Repetitions:		9[1]		
		Replicate Analyses		
Al (g/100 g)[2]	2.9	2.5	2.2	2.2
Ca "	32	23	19	15
Fe "	2.8	2.4	1.9	1.9
K "	0.50	0.37	0.35	0.38
Mg "	0.46	0.44	0.39	0.34
Na "	0.14	0.08	0.09	0.07
Si "	5.8	4.9	4.3	5.3
SO_4 "	8.5	7.5	6.5	6.4
Ti "	0.18	0.15	0.14	0.14
Ag (mg/kg)[3]	6.2	2.4	<0.42	<0.42
B "	390	470	390	290
Ba "	160	100	86	93
Be "	14	13	10	11
Cd "				
Cl "	320	100	100	100
Co "	9.2	6.0	3.6	3.6
Cu "	73	94	88	75
Cu "	27	60	67	39
F "	290	390	270	300
Li "	39	12	7.5	8.9
Mn "	290	280	190	250
Mo "	7.4	4.4	0.86	2.3
Ni "	16	14	12	13
Sr "	260	50	52	53
V "	51	34	28	28
Zn "	34	29	26	27

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[1] Cumulative volume-per-mass ratio: 100 mL H_2O per gram of waste.

[2] g species per 100 g solid sample.

[3] mg species per kg solid sample.

Li, and V. The Georgetown waste showed leaching of higher percentages of Fe, K, Na, Ti, Ag, Ba, Be, Co, Li, Mn, Mo, Ni, and Sr than Alliance AFBC waste.

C.3.5 Proximate and Ultimate Analysis

Ultimate and proximate analyses were performed on the same feedstock and waste material as was included in the solid sample chemical analysis. The results are reported on a dry basis. Heating value (Btu/lb) is reported with results of the proximate analyses. Percent fixed carbon (proximate analysis) and percent oxygen (ultimate analysis) are calculated by difference.

Ultimate and proximate analyses of the Exxon PFBC feedstock materials were performed to determine the possible source of components of the combustion wastes (Table C-25). The feed coal is the likely source of the sulfur and carbon that will be ashed. The analyses of the PFBC waste streams (Table C-26) indicates wastes from incomplete combustion in the third cyclone material which retained 89 Btu/lb heating value. These analyses also indicate that the highest sulfur content in the solid wastes is in the bed materials. Comparison of the ultimate and proximate analyses of leached and unleached PFBC mixed waste (Table C-27) shows that about 15% of the ash and about half the sulfur is removed during leaching.

The ultimate and proximate analyses show that the Alliance AFBC mixed waste (Table C-28) was not completely combusted. About 10% of the ash was dissolved during leaching and about half the sulfur present in the unleached waste is dissolved during leaching.

C.4 Solids Composition of Disposal Media

C.4.1 Microscopic Examinations

A geological description of the composition of the disposal media was obtained by examining the media with a binocular microscope. The glacial till, a tan material, was composed of about one-third limestone and two-thirds

TABLE C-25. ULTIMATE AND PROXIMATE ANALYSES OF PFBC FEEDSTOCK MATERIALS

	Feed Coal	Feed Dolomite
Proximate:		
Btu/lb	12049	0
% Ash	9.80	58.13
% Volatile	39.92	45.40
% Fixed Carbon	50.28	–
Ultimate:		
% Carbon	68.10	12.45
% Hydrogen	4.97	0.01
% Nitrogen	1.06	0.14
% Sulfur	4.20	0.02
% Oxygen	11.87	29.35

TABLE C-26. ULTIMATE AND PROXIMATE ANALYSES OF PFBC WASTE STREAMS

	Bed Draw Composite (Runs 79 and 80)	Second Cyclone Composite (Runs 79 and 80)	Third Cyclone Composite (Runs 80 and 81)
Proximate:			
Btu/lb	0	0	89
% Ash	98.52	98.94	96.62
% Volatile	1.72	0.92	4.90
% Fixed Carbon	–	0.14	–
Ultimate:			
% Carbon	0.70	0.08	0.36
% Hydrogen	0.09	0.01	0.19
% Nitrogen	0.08	0.14	0.12
% Sulfur	11.10	6.17	5.86
% Oxygen	–	–	–

TABLE C-27. ULTIMATE AND PROXIMATE ANALYSES OF UNLEACHED AND LEACHED PFBC MIXED WASTE

	Unleached	Leached	
		Replicate Analyses	
Proximate:			
Btu/lb	0	0	0
% Ash	98.46	83.24	84.97
% Volatile	1.77	17.77	15.58
% Fixed Carbon	-	-	-
Ultimate:			
% Carbon	0.60	0.90	0.18
% Hydrogen	0.09	1.72	1.61
% Nitrogen	0.11	0.09	0.15
% Sulfur	9.62	5.96	5.59
% Oxygen	-	8.09	7.50

TABLE C-28. ULTIMATE AND PROXIMATE ANALYSES OF UNLEACHED AND LEACHED ALLIANCE AFBC MIXED WASTE

	Unleached	Leached	
		Replicate Analyses	
Proximate:			
Btu/lb	38	325	332
% Ash	88.16	77.75	76.61
% Volatile	25.20	35.30	36.11
% Fixed Carbon	-	-	-
Ultimate:			
% Carbon	5.07	7.01	7.32
% Hydrogen	0.66	1.38	1.38
% Nitrogen	0.14	0.26	0.23
% Sulfur	7.60	4.26	5.26
% Oxygen	-	9.34	9.20

siltstone, mudstone, granite, schist, mica, dolomite, sandstone, quartz, and iron concretions. The till also contained a small amount (probably less than 5%) of plant material.

The alluvium ranged from tan to a brown in color. The major component appeared to be quartz with about 5% mica, siltstone, iron concretion grains, coal, limestone, dolomite, calcite, carbonate conglomerate, marble, and sandstone.

The interburden was dark grey. Slightly more than half of this material appeared to be quartz, with the other major component being mica. There was a small amount (<5%) of tourmaline and gypsum. The interburden material contained about 40% coal fragments in the sample examined.

The sandstone contained three distinctly different materials. One type, a white sandstone, appeared to be about 95% quartz with some muscovite and white cement. The second type of sandstone in the sample was a dark grey material composed of organic material (plant impressions) with quartz and mica. The third type of sandstone was a silver grey material that was about 80% quartz but also contained biotite, muscovite, and opaque minerals.

The shale disposal media also contained three distinctly different materials. The first type, a tan material, was about 90% quartz, with some mica, iron oxide, and an unidentified black mineral. The second shale type, a grey material, contained a large amount (>95%) of white, translucent, quartz, with a trace of the same unidentified black material observed in the first type. The third shale type was a dark grey material composed primarily of quartz with some muscovite and hematite and the same unidentified black mineral seen in the other two shale types.

A thin section of the limestone disposal media was examined with a polarizing microscope. The dark olive grey material contained sparry calcite and fossiliferous pellet rock.

C.4.2 X-Ray Diffraction Analysis

The mineralogic composition of the disposal media was also determined from X-ray diffraction patterns produced from ground specimens of representative portions of each medium. The representative samples were obtained by the standard method of coning and quartering. X-ray analysis of the media provided an overall view of the mineral species present in each medium. However, because these materials were natural composites of several minerals, the complexity of the X-ray pattern precluded unquestionable identification of all mineral fractions.

The mineral components identified in each of the disposal media are shown in Table C-29. The diffraction patterns of the shale, interburden, and sandstone samples exhibited similar complex diffraction patterns. The same mineral components appeared to be present in slightly different quantities in the three media. The major crystalline component was quartz. The X-ray patterns were also compatible with chlorite, diopside, enstatite, augite, vermiculite, nontronite, phlogopite, muscovite, kaolinite, illite, and montmorillonite. Additional analysis of clay fractions would be required to determine the individual clay mineral components that were present. Samples of sandstone and shale contained the same mineral components before and after leaching with deionized water.

The alluvium sample contained quartz as a major component and a moderate amount of muscovite. Albite was also probably present in small amounts.

The crystalline components identifiable by X-ray powder diffraction of the Greer limestone and the glacial till were quartz in major quantity, calcite in moderate amounts, and dolomite in minor amounts. From the solids analysis, several mineral components in the Greer limestone sample and the glacial till sample were tentatively identified. Barium muscovite, phlogopite and trioctahedral illite were probably present in trace amounts.

TABLE C-29. MINERAL COMPONENTS IDENTIFIED IN THE DISPOSAL MEDIA

Medium	Mineral Group	Mineral Name	Approximate Chemical Formula
Shale	Silica	Quartz (low)	SiO_2
	Clay	Kaolinite	$Al_2Si_2O_5(OH)_4$
	Clay	Montmorillinite	$Ca \cdot Na \cdot Mg \cdot Fe \cdot Al \cdot Si \cdot O \cdot OH \cdot H_2O$
	Clay	Vermiculite	$Mg \cdot Fe \cdot X \cdot Al \cdot Si \cdot O \cdot OH \cdot H_2O$
	Clay	Illite	$K \cdot Na \cdot Ca \cdot Mg \cdot Al \cdot Fe \cdot Ti \cdot Si \cdot O$
	Clay	Nontronite	$Fe \cdot Al \cdot Si \cdot Al \cdot O \cdot OH$
	Phyllosilicate	Chlorite	$Na \cdot K \cdot Ca \cdot Mg \cdot Al \cdot Si \cdot O \cdot OH \cdot H_2O$
	Mica	Phlogopite	$K \cdot Mg_3(Si_3AlO_{10})(OH)_2$
	Mica	Muscovite	$K \cdot Na \cdot Al \cdot Mg \cdot Fe \cdot Si \cdot Al \cdot O \cdot OH$
	Pyroxene	Enstatite	$(Mg, Fe)SiO_3$
	Pyroxene	Diopside	$Ca\ Mg\ (SiO_3)_2$
	Pyroxene	Augite	$(Ca, Fe, Mg)SiO_3$
Interburden	Silica	Quartz (low)	SiO_2
	Clay	Kaolinite	$Al_2Si_2O_5(OH)_4$
	Clay	Montmorillonite	$Ca \cdot Na \cdot Mg \cdot Fe \cdot Al \cdot Si \cdot O \cdot OH \cdot H_2O$
	Clay	Vermiculite	$Mg \cdot Fe \cdot X \cdot Al \cdot Si \cdot O \cdot OH \cdot H_2O$
	Clay	Illite	$K \cdot Na \cdot Ca \cdot Mg \cdot Al \cdot Fe \cdot Ti \cdot Si \cdot O$
	Clay	Nontronite	$Fe \cdot Al \cdot Si \cdot Al \cdot O \cdot OH$
	Clay	Chlorite	$Na \cdot K \cdot Ca \cdot Mg \cdot Al \cdot Si \cdot O \cdot OH \cdot H_2O$
	Mica	Phlogopite	$K\ Mg_3(Si_3AlO_{10})(OH)_2$
	Mica	Muscovite	$K \cdot Na \cdot Al \cdot Mg \cdot Fe \cdot Si \cdot Al \cdot O \cdot OH$
	Pyroxene	Enstatite	$(Mg,Fe)SiO_3$
	Pyroxene	Diopside	$Ca\ Mg\ (SiO_3)_2$
	Pyroxene	Augite	$(Ca, Fe, Mg)SiO_3$
Sandstone	Silica	Quartz (low)	SiO_2
	Clay	Kaolinite	$Al_2Si_2O_5(OH)_4$
	Clay	Montmorillonite	$Ca \cdot Na \cdot Mg \cdot Fe \cdot Al \cdot Si \cdot O \cdot OH \cdot H_2O$
	Clay	Vermiculite	$Mg \cdot Fe \cdot X \cdot Al \cdot Si \cdot O \cdot OH \cdot H_2O$

(Continued)

TABLE C-29. MINERAL COMPONENTS IDENTIFIED IN THE DISPOSAL MEDIA (Continued)

Medium	Mineral Group	Mineral Name	Approximate Chemical Formula
Sandstone (continued)	Clay	Illite	$K\cdot Na\cdot Ca\cdot Mg\cdot Al\cdot Fe\cdot Ti\cdot Si\cdot O$
	Clay	Nontronite	$Fe\cdot Al\cdot Si\cdot Al\cdot O\cdot OH$
	Mica	Phlogopite	$K\ Mg_3(Si_3AlO_{10})(OH)_2$
	Mica	Muscovite	$K\cdot Na\cdot Al\cdot Mg\cdot Fe\cdot Si\cdot Al\cdot O\cdot OH$
	Pyroxene	Enstatite	$(Mg,Fe)SiO_3$
	Pyroxene	Diopside	$CaMg(SiO_3)_2$
	Pyroxene	Augite	$(Cu,Fe,Mg)SiO_3$
Glacial Till	Silica	Quartz (low)	SiO_2
	Clay	Illite	$K\cdot Na\cdot Ca\cdot Mg\cdot Al\cdot Fe\cdot Ti\cdot Si\cdot O$
	Clay	Chlorite	$Na\cdot K\cdot Ca\cdot Mg\cdot Al\cdot Si\cdot O\cdot OH\cdot H_2O$
	Mica	Phlogopite	$K\ Mg_3(Si_3AlO_{10})(OH)_2$
	Carbonate	Calcite	$CaCO_3$
	Carbonate	Dolomite	$CaMg(CO_3)_2$
Alluvium	Silica	Quartz (low)	SiO_2
	Feldspar (plagioclase series)	Albite	$NaAlSi_3O_8$
	Mica	Muscovite	$K\cdot Na\cdot Al\cdot Mg\cdot Fe\cdot Si\cdot Al\cdot O\cdot OH$
Limestone	Silica	Quartz (low)	SiO_2
	Clay	Illite	$K\cdot Na\cdot Ca\cdot Mg\cdot Al\cdot Fe\cdot Ti\cdot Si\cdot O$
	Mica	Phlogopite	$K\ Mg_3(Si_3AlO_{20})(OH)_2$
	Carbonate	Calcite	$CaCO_3$
	Carbonate	Dolomite	$CaMg(CO_3)_2$

C.4.3 Chemical Analysis of Solid Samples

Samples of disposal media were digested by the same methods that were used for the FBC waste. The same chemical parameters and methods of analysis were also used. Samples of each disposal medium were analyzed as obtained. In addition, samples that had been exposed to Exxon PFBC waste leachate and leachate from Alliance AFBC waste were analyzed. The analytical results for the shale, interburden, sandstone, glacial till, alluvium, and limestone are shown in Tables C-30 to C-35.

The final higher cumulative volume-per-mass ratio for media exposed to Alliance AFBC waste leachate may account for the higher concentrations of contaminants observed than were seen in the media exposed to Exxon PFC waste leachate.

For the shale medium, no significant differences in concentrations of Fe, K, Na, Si, and Ti were observed after exposure to Alliance AFBC waste leachate or Exxon PFBC waste leachate. Uniform gain of calcium and sulfate was observed when shale was exposed to either waste leachate (Table C-30). Aluminum decreased while magnesium increased slightly in the shale after exposure to Alliance AFBC waste leachate only. While no extreme differences were observed in the trace metal content of shale before and after exposure to Exxon PFBC waste leachate, concentrations of Cl, Co, Cr, Mn, Mo, and especially Sr increased in the shale after exposure to Alliance AFBC waste leachate.

Interburden solids analyzed before and after exposure to the same waste leachates showed uniform increases in calcium and sulfate content while silicon concentration decreased after leachate exposure (Table C-31). Concentrations of Fe, K, Mg, and Ti in the interburden were not greatly affected by leachate exposure. Sodium and aluminum decreased in the solids after exposure to Alliance AFBC waste leachate only. Trace metal concentrations in the interburden after exposure to the waste leachates usually varied up or down from the original interburden concentrations. While barium and maganese concentrations were fairly constant, beryllium, vanadium, and zinc cnocentrations decreased and Co, Cu, F, Li, and Ni increased in the solids after exposure to

TABLE C-30. SOLIDS ANALYSIS OF SHALE BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000008		A576108		A579308	
Description:	Shale Disp. Medium		Shale Disp. Medium		Shale Disp. Medium	
Leachate:	None		Exxon PFBC		Alliance AFBC	
Protocol Step:	—		5		5	
Leaching Time:	—		7d		7d	
No. Repetitions:	—		6[1]		9[2]	
	Replicate Analyses		Replicate Analyses		Replicate Analyses	
Al (g/100 g)[3]	9.4	9.4	8.4	-	7.2	6.9
Ca "	1.14	1.10	4.2	4.2	3.7	3.5
Fe "	4.4	4.1	4.0	4.0	4.3	4.2
K "	2.8	2.7	2.4	2.4	2.4	2.3
Mg "	0.84	0.85	0.77	-	1.05	1.00
Na "	0.31	0.31	0.30	0.81	0.32	0.27
Si "	25	24	22	22	21	20
SO_4 "	0.36	0.37	2.5	2.6	3.03	3.11
Ti "	0.56	0.53	0.50	0.50	0.65	0.62
Ag (mg/kg)[4]	<0.250	<0.250	-	-	-	-
B "	55	1250	410	870	290	470
Ba "	500	500	521	570	641	529
Be "	7.7	7.3	7.5	7.7	4.7	4.5
Cd "	0.13	0.13	-	-	-	-
Cl "	<40	<40	<40	<40	66	64
Co "	20	20	29	30	33	32
Cr "	84	79	82	84	93	91
Cu "	38	36	38	40	47	10
F "	560	550	540	560	570	550
Li "	50	60	75	-	65	65
Mn "	771	734	696	720	830	825
Mo "	<2.35	<2.34	<2.34	-	28	28
Ni "	48	49	40	-	57	54
Sr "	160	170	168	179	308	293
V "	140	128	119	118	115	114
Zn "	95	94	84	-	97	94

[1] Cumulative volume-per-mass ratio: 70 mL leachate per gram of shale.
[2] Cumulative volume-per-mass ratio: 100 mL leachate per gram of shale.
[3] g species per 100 g solid sample.
[4] mg species per kg solid sample.

TABLE C-31. SOLIDS ANALYSIS OF INTERBURDEN BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000009		A576109		A579309	
Description:	Interburden Disp. Medium		Interburden Disp. Medium		Interburden Disp. Medium	
Leachate:	None		Exxon PFBC		Alliance AFBC	
Protocol Step:	—		5		5	
Leaching Time:	—		7d		7d	
No. Repetitions:	—		6[1]		9[2]	
	Replicate Analyses		Replicate Analyses		Replicate Analyses	
Al (g/100 g)[3]	9.8	9.9	8.8	9.0	7.7	7.7
Ca "	0.50	0.57	2.88	2.83	2.5	2.3
Fe "	2.4	2.2	2.0	1.9	2.4	2.5
K "	1.64	1.68	1.41	1.42	1.44	1.41
Mg "	0.40	0.40	0.36	0.37	0.47	0.47
Na "	0.63	0.74	0.76	0.58	0.23	0.21
Si "	18.5	18.9	16.6	16.7	16.7	16.5
SO_4 "	0.66	0.62	2.3	2.2	2.42	2.48
Ti "	0.53	0.54	0.47	0.48	0.64	0.64
Ag (mg/kg)[4]	<0.250	<0.250	-	-	-	-
B "	265	170	330	410	340	420
Ba "	1148	771.5	757.0	727	870	857
Be "	5.8	5.7	5.0	4.7	3.1	3.1
Cd "	0.18	0.20	-	-	-	-
Cl "	<40	195	<40	<40	70	79
Co "	<14.3	<14.7	19	25	35	37
Cr "	102	104	19.1	25	102	100
Cu "	50	53	40	51	27	39
F "	300	290	270	280	250	290
Li "	125	125	100	105	115	120
Mn "	58	65	56	55	63	62
Mo "	<2.33	<2.35	<2.34	<2.35	27	27
Ni "	58	59	64	52	72	76
Sr "	173	179	156	155	284	292
V "	145	145	117	118	115	120
Zn "	90	91	77	77	86	71

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[1] Cumulative volume-per-mass ratio: 70 mL leachate per gram of interburden.

[2] Cumulative volume-per-mass ratio: 100 mL leachate per gram of interburden.

[3] g species per 100 g solid sample.

[4] mg species per kg solid sample.

TABLE C-32. SOLIDS ANALYSIS OF SANDSTONE BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.	A000010		A576110		A579310	
Description	Sandstone Disp. Medium		Sandstone Disp. Medium		Sandstone Disp. Medium	
Leachate	None		Exxon PFBC		Alliance AFBC	
Protocol Step	—		5		5	
Leaching Time	—		7d		7d	
No. Repetitions	—		6[1]		9[2]	
	Replicate Analyses		Replicate Analyses		Replicate Analyses	
Al (g/100 g)[3]	9.5	9.5	7.9	8.1	6.8	7.0
Ca "	0.38	0.39	2.5	3.1	2.5	2.9
Fe "	4.2	4.3	3.4	3.4	4.1	3.7
K "	2.9	3.1	2.3	2.4	2.4	2.4
Mg "	0.75	0.74	0.61	0.62	0.88	0.86
Na "	0.32	0.28	0.32	0.91	0.32	0.33
Si "	26	26	25	25	25	24
SO_4 "	0.55	0.51	2.3	2.8	3.1	3.4
Ti "	0.46	0.48	0.40	0.41	0.55	0.55
Ag (mg/kg)[4]	<0.250	<0.250	–	–	–	–
B "	430	70	520	820	760	840
Ba "	539	523	954	1008	1268	1463
Be "	8.6	8.9	7.1	7.0	4.4	4.2
Cd "	0.13	0.10	–	–	–	–
Cl "	<40	69	<40	<40	67	77
Co "	<14.9	<14.6	15.5	26.0	30.0	28.3
Cr "	77.4	79.3	67.9	67.2	75.3	76.7
Cu "	37	44	30.0	33.15	47.6	19.7
F "	500	470	370	400	320	450
Li "	70	65	50	70	90	90
Mn "	493	543	413	408	464	452
Mo "	<2.35	<2.35	<2.35	<2.33	26	24
Ni "	44	42	50	40	53	49
Sr "	106	108	104	115	209	218
V "	142	143	100	100	98	102
Zn "	93	91	73	75	69	77

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[1] Cumulative volume-per-mass ratio: 70 mL leachate per gram of sandstone.
[2] Cumulative volume-per-mass ratio: 200 mL leachate per gram of sandstone.
[3] g species per 100 g solid sample.
[4] mg species per kg solid sample.

TABLE C-33. SOLIDS ANALYSIS OF GLACIAL TILL BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000012		A576112		A579312	
Description:	Glacial Till Disp. Medium		Glacial Till Disp. Medium		Glacial Till Disp. Medium	
Leachate:	None		Exxon PFBC		Alliance AFBC	
Protocol Step:	—		5		5	
Leaching Time:	—		7d		7d	
No. Repetitions:	—		6[1]		9[2]	
	Replicate Analyses		Replicate Analyses		Replicate Analyses	
Al (g/100 g)[3]	6.2	6.2	5.8	5.7	4.6	4.7
Ca "	5.6	5.7	8.3	8.3	7.6	7.4
Fe "	3.4	3.4	3.0	3.0	3.7	3.7
K "	2.4	2.4	2.1	2.1	2.2	2.2
Mg "	1.7	1.7	1.6	1.6	2.1	2.0
Na "	0.47	0.45	0.39	0.43	0.43	0.39
Si "	23	23	21	21	20	20
SO_4 "	<0.1	<0.1	2.2	2.2	2.6	2.8
Si "	0.37	0.36	0.33	0.32	0.44	0.45
Ag (mg/kg)[4]	<0.250	<0.250	-	-	-	-
B "	140	100	550	440	310	400
Ba "	295	304	384	338	327	337
Be "	6.0	5.8	5.3	5.3	2.7	2.8
Cd "	0.15	0.15	-	-	-	-
Cl "	50	45	43	69	0.92	99
Co "	15.7	<15.1	15.1	19.7	22.5	22.4
Cr "	65	66	65	63	60	62
Cu "	44	45	33	33	115	67
F "	510	590	540	510	490	170
Li "	20	20	40	40	50	50
Mn "	543	506	455	466	512	487
Mo "	16	12	16	15	36	38
Ni "	49	47	45	44	55	56
Sr "	127	127	128	133	305	313
V "	141	142	108	106	93	101
Zn "	88	86	79	76	86	88

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[1] Cumulative volume-per-mass ratio: 70 mL leachate per gram of glacial till.

[2] Cumulative volume-per-mass ratio: 100 mL leachate per gram of glacial till.

[3] g species per 100 g solid sample.

[4] mg species per kg solid sample.

TABLE C-34. SOLIDS ANALYSIS OF ALLUVIUM BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000013		A576113		A579113	
Description:	Alluvium Disp. Medium		Alluvium Disp. Medium		Alluvium Disp. Medium	
Leachate:	None		Exxon PFBC		Alliance AFBC	
Protocol Step:	—		5		5	
Leaching Time:	—		7d		7d	
No. Repetitions:	—		6[1]		9[2]	
	Replicate Analyses		Replicate Analyses		Replicate Analyses	
Al (g/100 g)[3]	4.1	4.1	3.9	3.9	3.0	3.1
Ca "	0.144	0.138	2.3	2.6	1.9	2.1
Fe "	3.0	3.0	2.7	2.7	3.2	3.3
K "	1.2	1.2	1.08	1.09	1.07	1.08
Mg "	0.30	0.30	0.29	0.29	0.36	0.38
Na "	0.36	0.38	0.95	0.93	0.34	0.44
Si "	35	35	32	32	32	32
SO_4 "	<0.1	<0.1	2.0	2.0	2.3	2.3
Ti "	0.39	0.38	0.35	0.35	0.48	0.52
Ag (mg/kg)[4]	<0.250	<0.250	-	-	-	-
B "	1510	570	510	1300	1400	980
Ba "	126	166	229	217	233	243
Be "	5.2	5.0	4.0	4.7	1.9	1.9
Cd "	0.11	0.10	-	-	-	-
Cl "	<40	<40	<40	45	104	104
Co "	<14.5	<14.9	17.3	26.9	18.1	20.1
Cr "	52	51	39	46	37	37
Cu "	28	31	25	36	38	46
F "	200	260	150	170	150	150
Li "	40	40	<2.5	20	43	45
Mn "	620	609	606	631	661	677
Mo "	<2.35	<2.34	<2.35	<2.35	13.3	14.5
Ni "	21	22	22	25	28	34
Sr "	69	71	84	79	170	175
V "	91	92	59	61	45	48
Zn "	50	51	47	48	53	47

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[1] Cumulative volume-per-mass ratio: 70 mL leachate per gram of alluvium.
[2] Cumulative volume-per-mass ratio: 100 mL leachate per gram of alluvium.
[3] g species per 100 g solid sample.
[4] mg species per kg solid sample.

TABLE C-35. SOLIDS ANALYSIS OF LIMESTONE BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000014		A576114		A579314	
Description:	Limestone Disp. Medium		Limestone Disp. Medium		Limestone Disp. Medium	
Leachates:	None		Exxon PFBC		Alliance AFBC	
Protocol Step:	—		5		5	
Leaching Time:	—		7d		7d	
No. Repetitions:	—		6[1]		9[2]	
	Replicate Analyses		Replicate Analyses		Replicate Analyses	
Al (g/100 g)[3]	1.47	1.46	1.44	1.40	1.34	1.26
Ca "	32	32	32	32	29	28
Fe "	0.72	0.72	0.70	0.70	0.83	0.80
K "	0.74	0.76	0.63	0.63	0.66	0.64
Mg "	1.09	1.08	1.08	1.05	1.52	1.45
Na "	0.139	0.119	0.125	0.122	0.145	0.403
Si "	4.1	4.1	4.0	4.0	4.5	4.31
SO_4 "	0.12	0.12	1.36	1.30	1.29	1.29
Ti "	0.108	0.107	0.099	0.099	0.144	0.133
Ag (mg/kg)[4]	<0.250	<0.250	–	–	–	–
B "	350	6	280	70	14	43
Ba "	68	51.3	171	185	224	163
Be "	1.9	1.8	<1.21	1.37	<0.119	<0.119
Cd "	0.12	0.13	–	–	–	–
Cl "	120	110	75	68	150	100
Co "	<14.6	<14.4	<15.1	<14.9	<1.48	1.53
Cr "	48	52	42	48	22	23
Cu "	26	30	119	25	139	102
F "	500	400	400	200	390	380
Li "	25	<2.5	20	<2.5	<2.5	<2.5
Mn "	182	182	173	173	183	188
Mo "	<2.35	<2.33	<2.35	<2.35	5	5
Ni "	15	16	14	16	16	17
Sr "	366	365	324	321	484	459
V "	86	92	56	66	14	20
Zn "	32	33	32	31	16	16

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[1] Cumulative volume-per-mass ratio: 70 mL leachate per gram of limestone.

[2] Cumulative volume-per-mass ratio: 100 mL leachate per gram of limestone.

[3] g species per 100 g solid sample.

[4] mg species per kg solid sample.

both waste leachates. Chromium and strontium concentrations decreased after exposure to PFBC waste leachate only. Nickel, molybdenum, and strontium increased in the interburden after exposure to Alliance AFBC waste leachate.

When sandstone was exposed to Exxon PFBC waste leachate and Alliance AFBC waste leachate, it showed increased calcium and sulfate content and decreased aluminum content (Table C-32). No significant differences in concentrations of Fe, K, Mg, Na, Si, and Ti were observed after the sandstone was exposed to either waste leachate. Of the trace metals in sandstone, Be, F, Mn, V, and Zn appeared to decrease with exposure to either waste leachate while boron, barium, and cobalt increased. Concentrations of lithium, chloride, and chromium decreased after exposure to Exxon PFBC waste leachate only; strontium, chloride, and molybdenum increased after exposure to Alliance AFBC waste leachate only.

For glacial till, calcium and sulfate concentrations increased after exposure to the waste leachates whereas aluminum decreased slightly (Table C-33). No significant changes were observed for Fe, K, Na, Si, and Ti concentrations in the till after exposure to either waste leachate. Magnesium concentration in the glacial till increased after exposure to Alliance AFBC waste leachate only. The trace metal behavior in the glacial till showed increases in boron, barium, and lithium and decreases in beryllium, manganese, and vanadium after exposure to both leachates. The till increased in concentrations of Sr, Ni, Cu, and Mo after exposure to Alliance AFBC waste leachate only and decreased in copper and zinc after exposure to PFBC waste leachate only.

Alluvium, when exposed to Exxon PFBC and Alliance AFBC waste leachate, showed large increases in concentrations of calcium and sulfate and slight decreases in aluminum and silicon content (Table C-34). When exposed to Exxon PFBC waste leachate only, alluvium decreased in iron concentration and increased in sodium. When exposed to Alliance AFBC waste leachate only, the alluvium increased in magnesium and titanium content. Of the trace metals, barium, cobalt, and strontium increased in the alluvium after exposure to both waste leachates and decreased in Be, Cr, F, and V. When exposed to Alliance AFBC waste leachate only, concentrations of nickel, molybdenum, and chloride increased. When exposed to PFBC waste leachate only, alluvium decreased in lithium and increased in cobalt concentrations.

When the limestone was exposed to Exxon PFBC waste leachate and Alliance AFBC waste leachate, no major changes occurred in the solids concentrations of Al, Ca, Fe, K, Na, Si, or Ti (Table C-35). Sulfate was higher in the solids after exposure to the waste leachates. Magnesium content was higher in the limestone after exposure to Alliance AFBC waste leachate only. Exposure to the waste leachates also resulted in increased barium and copper content and decreased Be, F, and V content in the limestone. When exposed to PFBC leachate only, manganese and chloride concentrations decreased. When exposed to Alliance AFBC waste leachate only, strontium and molybdenum increased while Zn and Cr decreased.

A comparison of behavior of the media showed that they all increased in calcium and sulfate concentrations when exposed to FBC leachates except limestone which did not increase in calcium content. While concentrations of Fe, K, and Ti were fairly constant, losses of Na, Al, and Si were observed for some of the media.

Elemental analysis of shale and sandstone after leaching are shown in Table C-36. The shale and sandstone compositions were similar before and after leaching with a few exceptions; the leached shale residue contained at least twice as much Ca, Cu, Mn, and Sr as the leached sandstone residue. The leached sandstone contained more barium than the leached shale residue. Both media lost boron and vanadium compounds from the solids with leaching.

C.4.4 Cation Exchange Capacity

The cation exchange capacities of the disposal media are shown in Table C-37. The sample exhibiting the greatest ability to exchange sodium ions was mine interburden. The other five media had approximately equal cation ex-

TABLE C-36. SOLIDS COMPOSITION OF SHALE AND SANDSTONE MEDIA AFTER LEACHING

Sample ID:		A277008			A277010	
Description:		No Waste			No Waste	
Protocol Step:		2			2	
Leaching Time:		7d			7d	
No. Repetitions:		7			7	
Elements/Species	Sample A	Sample B	Average	Sample A	Sample B	Average
Al (g/100 g)[1]	8.41	8.11	8.2	7.31	7.9	7.6
Ca "	1.0	9.2	5.1	0.16	0.17	0.16
Fe "	5.1	4.9	5.0	4.5	4.9	4.7
K "	2.4	2.2	2.3	2.1	2.3	2.2
Mg "	1.0	1.0	1.0	0.72	0.72	0.72
Na "	0.41	0.36	0.39	0.34	0.32	0.33
Si "	25	24	24	26.0	25.0	26.0
SO_4 "						
Ti "	0.54	0.52	0.53	0.43	0.46	0.45
Ag (mg/kg)[2]	<0.42	<0.42	<0.42	6.3	8.3	7.3
B "	131	300	130	160	210	180
Ba "	560	550	555	1200	950	1080
Be "	25	26	26	27	28	28
Cd "						
Cl "						
Co "	25	27	26	27	28	28
Cr "	130	120	125	100	110	105
Cu "	57	39	48	14	37	26
F "						
Li "	52	53	52			
Mn "	880	810	845	460	470	465
Mo "	17	17	17	20	20	20
Ni "	45	48	46	47	49	48
Sr "	170	160	165	89	94	92
V "	100	110	105	110	110	110
Zn "	120	120	120	110	110	110

[1] g species per 100 g solid sample.
[2] mg species per kg solid sample.

change capacities. If the sorption of contaminants from FBC wastes were controlled only by cation-exchange mechanisms, the mine interburden should be superior to the other media in sorbing the trace metals and other mobile cations.

TABLE C-37. CATION EXCHANGE CAPACITIES OF DISPOSAL MEDIA

Disposal Medium	Cation Exchange Capacity (meq/100 g)[1]
Shale	36.1
Interburden	50.5
Sandstone	31.4
Glacial Till	35.6
Alluvium	37.0
Limestone	30.0

[1] The cation exchange capacity has been determined using a method of sodium saturation. These results are reported in milliequivalents per 100 g.

The cation-exchange capacity is actually a measure of the degree of substitution of cations on surface layers of the mineral structures in the media. Exchangeable cations are sorbed to mineral surfaces to compensate for positive charge deficits in the interior mineral layers created by atoms of lower positive valence replacing higher valence atoms. In water, the exchangeable cations on the mineral surfaces can easily be exchanged for other cations present in solution. The extent of the cation-exchange capacity is influenced by particle size, crystallinity, and residence time of exchangeable cation solution. Generally, the positive ions in the interlayers become increasingly replaceable with decreasing particle size, decreasing crystallinity, and increased exposure to aqueous cationic species. Cation exchange capacity can be reduced by large ions (aluminum and hydrates of Fe_2O_3) capable of clogging access to reactive sites.

C.4.5 Proximate and Ultimate Analysis

The proximate and ultimate analysis of the disposal media both prior to and after exposure to leachate were determined. These analyses were performed primarily to determine the amount of ash that was leached. The shale did not lose much ash when exposed to FBC waste leachate, and it sorbed sulfur from the waste leachate (Table C-38). The interburden had a lower ash content than the shale and more sulfur, so it apparently contributed sulfur to the Exxon PFBC leachate during leaching, and did not sorb any sulfur from the Alliance waste (Table C-39). The sandstone was similar to the shale in percent ash, with slightly higher sulfur (Table C-40). It also sorbed a little sulfur from both waste leachates. The glacial till and alluvium had the lowest sulfur content in the unleached media and sorbed sulfur from the waste leachates (Tables C-41 and C-42). The ash content of the till was a little lower than the alluvium. The lowest ash content was observed from the limestone medium (Table C-43).

TABLE C-38. PROXIMATE ANALYSIS OF SHALE BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000008	A576108		A579308	
	Disp. Medium	Disp. Medium		Disp. Medium	
Leachate:	None	Exxon PFBC		Alliance AFBC	
Protocol Step:	—	5		5	
Leaching Time:	—	7d		7d	
No. Repetitions:	—	6[1]		9[2]	
		Replicate Analyses		Replicate Analyses	
Proximate					
Btu/lb	254	196	247	199	203
% Ash	90.00	90.26	86.63	89.42	89.32
% Volatile	10.35	13.17	13.72	13.74	13.53
% Fixed Carbon	-	-	-	-	-
Ultimate					
% Carbon	3.12	3.45	3.53	3.19	2.99
% Hydrogen	0.73	0.85	0.95	0.75	0.77
% Nitrogen	0.26	0.15	0.32	0.23	0.20
% Sulfur	0.70	1.26	1.11	1.18	1.26
% Oxygen	5.19	4.03	4.30	5.23	5.46

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[1] Cumulative volume-per-mass ratio: 70 mL leachate per g shale.

[2] Cumulative volume-per-mass ratio: 100 mL leachate per g shale.

TABLE C-39. PROXIMATE ANALYSIS OF INTERBURDEN BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000009	A576109		A579309	
	Disp. Medium	Disp. Medium		Disp. Medium	
Leachate:	None	Exxon PFBC		Alliance AFBC	
Protocol Step:	—	5		5	
Leaching Time:	—	7d		7d	
No. Repetitions:	—	6[1]		9[2]	
		Replicate Analyses		Replicate Analyses	
Proximate					
Btu/lb	3052	3352	3172	2984	3176
% Ash	70.66	70.66	70.28	71.65	72.93
% Volatile	15.15	17.61	18.37	16.74	16.92
% Fixed Carbon	14.19	11.73	11.35	11.61	10.15
Ultimate					
% Carbon	18.87	19.96	20.01	17.81	18.56
% Hydrogen	1.80	2.01	1.86	1.81	1.72
% Nitrogen	0.43	0.56	0.56	0.44	0.32
% Sulfur	2.30	1.98	1.85	2.35	2.42
% Oxygen	5.94	4.83	5.44	5.94	4.05

[1] Cumulative volume-per-mass ratio: 70 mL leachate per g interburden.

[2] Cumulative volume-per-mass ratio: 200 mL leachate per g interburden.

TABLE C-40. PROXIMATE ANALYSIS OF SANDSTONE BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000010 Disp. Medium	A576110 Disp. Medium		A579310 Disp. Medium	
Leachate:	None	Exxon PFBC		Alliance AFBC	
Protocol Step:	—	5		5	
Leaching Time:	—	7d		7d	
No. Repetitions:	—	6[1]		9[2]	
		Replicate Analyses		Replicate Analyses	
Proximate					
Btu/lb	156	157	303	112	140
% Ash	92.43	93.35	92.64	92.94	92.43
% Volatile	8.13	9.76	10.29	10.70	12.20
% Fixed Carbon	-	-	-	-	-
Ultimate					
% Carbon	1.71	1.77	1.85	2.08	2.11
% Hydrogen	0.57	0.53	0.59	0.60	0.61
% Nitrogen	0.54	0.38	0.20	0.20	0.18
% Sulfur	1.37	1.74	1.84	1.96	1.77
% Oxygen	3.38	2.23	-	2.22	2.90

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[1] Cumulative volume-per-mass ratio: 70 mL leachate per g sandstone.

[2] Cumulative volume-per-mass ratio: 100 mL leachate per g sandstone.

TABLE C-41. PROXIMATE ANALYSIS OF GLACIAL TILL BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000012 Disp. Medium	A576112 Disp. Medium		A579312 Disp. Medium	
Leachate:	None	Exxon PFBC		Alliance AFBC	
Protocol Step:	—	5		5	
Leaching Time:	—	7d		7d	
No. Repetitions:	—	6[1]		9[2]	
		Replicate Analyses		Replicate Analyses	
Proximate					
Btu/lb	0	0	0	0	241
% Ash	87.86	86.56	87.83	86.83	86.56
% Volatile	13.73	15.11	15.20	15.55	15.08
% Fixed Carbon	-	-	-	-	-
Ultimate					
% Carbon	2.90	2.70	2.72	2.87	2.63
% Hydrogen	0.43	0.54	0.47	0.52	0.54
% Nitrogen	0.17	0.18	0.15	0.15	0.18
% Sulfur	0.06	0.53	0.43	0.82	0.96
% Oxygen	8.58	9.49	8.40	8.81	9.13

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[1] Cumulative volume-per-mass ratio: 70 mL leachate per g glacial till.

[2] Cumulative volume-per-mass ratio: 100 mL leachate per g glacial till.

TABLE C-42. PROXIMATE ANALYSIS OF ALLUVIUM BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000013	A576113		A579113	
	Disp. Medium	Disp. Medium		Disp. Medium	
Leachate:	None	Exxon PFBC		Alliance AFBC	
Protocol Step:	—	5		5	
Leaching Time:	—	7d		7d	
No. Repetitions:	—	6[1]		9[2]	
		Replicate Analyses		Replicate Analyses	
Proximate					
Btu/lb	0	0	0	0	0
% Ash	97.62	96.74	96.83	95.82	96.42
% Volatile	2.67	4.04	3.80	4.62	4.00
% Fixed Carbon	-	-	-	-	-
Ultimate					
% Carbon	0.11	0.13	0.10	0.11	0.10
% Hydrogen	0.27	0.25	0.28	0.31	0.26
% Nitrogen	0.11	0.20	0.32	0.12	0.26
% Sulfur	0.05	0.42	0.44	0.75	0.65
% Oxygen	1.84	-	2.03	2.89	2.31

[1] Cumulative volume-per-mass ratio: 70 mL leachate per g alluvium.
[2] Cumulative volume-per-mass ratio: 100 mL leachate per g alluvium.

TABLE C-43. PROXIMATE ANALYSIS OF LIMESTONE BEFORE AND AFTER EXPOSURE TO FBC LEACHATE

Sample I.D.:	A000014 Disp. Medium	A576114 Disp. Medium		A579314 Disp. Medium	
Leachate:	None	Exxon PFBC		Alliance AFBC	
Protocol Step:	—	5		5	
Leaching Time:	—	7d		7d	
No. Repetitions:	—	6[1]		9[2]	
		Replicate Analyses		Replicate Analyses	
Proximate					
Btu/lb	0	0	0	0	0
% Ash	63.55	68.00	68.03	64.35	64.30
% Volatile	27.10	33.70	32.08	29.06	29.30
% Fixed Carbon	9.35	-	-	6.59	6.40
Ultimate					
% Carbon	10.00	9.22	9.09	9.61	9.68
% Hydrogen	0.08	0.16	0.10	0.11	0.12
% Nitrogen	0.11	0.11	0.11	0.11	0.14
% Sulfur	0.25	0.38	0.44	0.51	0.50
% Oxygen	26.01	22.13	22.23	25.31	25.26

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[1] Cumulative volume-per-mass ratio: 70 mL leachate per g limestone.

[2] Cumulative volume-per-mass ratio: 100 mL leachate per g limestone.